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A role of catalysis for the destruction of waste from the nuclear industry

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Abstract

Recent advances in application of catalysis to problems of waste destruction and off-gas treatment in the nuclear industry are presented: destruction of mixed organic wastes in a fluidized catalyst bed, mixed waste oxidation in catalytically active molten salts, selective catalytic reduction of NO_x, in off-gases, catalytic oxidation of H_2 in the ventilation exhaust from liquid waste tanks and catalytic removal of VOCs in processes of groundwater and soil remediation. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nuclear energy is considered to be environmentally clean because nuclear power plants do not produce atmospheric pollutants, such as sulfur oxides, nitrogen oxides and other harmful emissions generated by power plants burning fossil fuel. On the other hand, production of nuclear fuel and generation of nuclear energy is accompanied with the formation of substantial amounts of radioactive wastes, which creates severe problems of their safe treatment and disposal. The wastes are formed during uranium ore mining and processing, production of nuclear fuel for power stations, reprocessing of spent fuel, nuclear weapons production, equipment decontamination and remediation of nuclear sites — practically in all branches and processes of the nuclear industry; and their quantity reaches millions of cubic meters [1,2].

The urgency of the nuclear waste problems has increased during the past decade due to disarmament accompanied by dismantling of warheads, reprocessing of weapons grade uranium and plutonium to fuel for power stations and a need to transition, decommission, deactivate and dispose of numerous former weapons facilities contaminated with radionuclides and hazardous materials [2].

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Table 1
Application of catalysis in radioactive waste processing

Type of waste	Method of processing or storage	Problem	Application of catalysis
Mixed organic waste	Incineration in flame	Air pollutants, radioactive aerosols	Alternative process—catalytic fluidized bed oxidation
Mixed organic waste	Molten salt oxidation	High temperature, corrosionand NO_x formation	Application of catalytically active melts
Mixed waste	Plasma arc destruction	High NO_x concentration up to 10 000 ppm	Selective catalytic reduction of NO_x
High level waste containing nitrates	Vitrification	High NO_x concentration over 10 000 ppm	Selective catalytic reduction of NO_x
High level waste containing nitrates	Vitrification	High NO_x concentration over 10 000 ppm	Reduction of nitrates to N_2 and NH_3 followed by catalytic NH_3 oxidation to N_2
Liquid high level waste	Storage in tanks	H_2formation at explosive concentrations	Catalytic oxidation of H_2
Contaminated soil and groundwater	Remediation of nuclear sites by stripping of soil and groundwater with air or steam	Formation of VOCs	VOC catalytic oxidation

Catalysis can be used as a powerful tool to solve environmental problems of nuclear waste storage, processing and disposal. Applications of catalysis, in particular processes of radioactive waste processing, are shown in Table 1.

Radioactive wastes are classified according to their origin — from defense or commercial sources, the level of activity — high level and low level wastes, and according to material type — spent nuclear fuel, transuranic waste, mixed organic waste, etc. [1].

A considerable fraction of nuclear wastes is so-called mixed wastes containing organic compounds and radionuclides. These wastes are presented by complex mixtures of hazardous organic compounds and radionuclides of U, Pu and their fission products. The total amount of the mixed waste accumulated in the USA from DOE site activities is 174 000 m^3, including 52 000 m^3 of liquids and 122 000 m^3 of solid waste [1].

These wastes represent a threat to the environment upon their storage and disposal because of the combination of flammability, explosiveness, toxicity and radioactivity, and they need to be treated prior to disposal. The most commonly used technique for destroying combustible hazardous wastes is flame incineration. Although incineration is an effective technique it has a major disadvantage of the formation of atmospheric pollutants: NO_x, CO, hydrocarbons and aerosol radioactive particles [3–5]. As will be shown further, catalytic processes can be used for efficient treatment of liquid and solid waste in new alternative nuclear waste treatment processes, e.g., catalytic fluidized bed waste destruction or waste processing in catalytically active molten salts.

In contemporary waste processing technologies using high temperatures, for example, flame incinerators, plasma arc furnaces or glass melters, the exhaust gas has extremely high content of NO_x, that must be removed from the gas before its discharge to the atmosphere, which is achieved most efficiently by selective catalytic reduction (SCR) of NO_x [6–8].

Storage of high level liquid wastes is accompanied by the formation of radiolysis-generated hydrogen which forms explosive mixtures with air [9–12]. Catalytic oxidation of hydrogen in the ventilation off gas ensures the safety of the liquid waste storage. Similar technology is very promising for the removal of explosive hydrogen–oxygen mixtures generated by radiolysis in the water cooled circuit of nuclear heat supply stations.

During soil remediation or groundwater cleaning at contaminated sites by air or steam stripping, vapors of volatile organic compounds (VOCs), including carbon tetrachloride, are formed. The most efficient method for VOCs removal is their oxidation over solid catalysts [13–16].

This paper presents recent advances in application of catalysis to problems of waste destruction and off-gas treatment in nuclear industry. Mainly the results of the research activities of the Boreskov Institute of Catalysis (BIC) in Russia and results of cooperation with Lawrence Livermore National

Laboratory in the USA in the frame of International Science and Technology Center (ISTC) projects will be presented and discussed according to the following five directions: (1) destruction of mixed organic wastes in a fluidized catalyst bed, (2) waste oxidation in catalytic molten salts, (3) SCR of high concentration of NO_x in off-gases, (4) catalytic oxidation of hydrogen generated by radiolysis, (5) catalytic removal of VOCs formed in processes of soil remediation and groundwater cleaning at contaminated sites.

2. Destruction of mixed organic wastes in a fluidized catalyst bed

One of the most urgent problems in the field of nuclear waste management is environmentally safe treatment and disposal of mixed organic wastes containing U, Pu and their fission products. They comprise lubricating and hydraulic fluids, extractants, solvents and dilutants, filters, ion-exchange resins, packages, plastic containers, work clothing and other organic materials [1,17,18]. The development of environmentally clean technology for destruction of these wastes is of great importance. The method of high-temperature flame (or plasma) incineration is hazardous for the environment because it leads to secondary waste streams, e.g., deteriorated refractories, and generation of air pollutants, such as nitrogen oxides, and sub-micron radioactive particles emitted into the atmosphere [3–5,19].

We have proposed a new technology for the environmentally clean treatment of mixed organic radioactive wastes, which is based on the catalytic oxidation of organic wastes [19–23]. In catalytic oxidation the fuel is totally oxidized by surface catalytic reactions at low temperatures without a flame, and this process is principally different from conventional flame combustion proceeding at high temperatures via radical-chain reactions. This results in complete conversion of fuel to products of total oxidation: CO_2 and H_2O and precludes the formation of nitrogen oxides.

In recent years catalytic combustion processes have been developed most intensively mainly because of the possibility to substantially reduce toxic emissions of CO, unburned hydrocarbons and nitrogen oxides [7,24–37]. For the treatment of mixed organic wastes, a method of flameless combustion of organic fuels and wastes in a fluidized catalyst bed developed in BIC was used [7,30–37]. The unique feature of this method of fuel and waste combustion is the possibility of total oxidation of organic compounds at nearly the stoichiometric ratio with oxygen at low temperatures (600–750°C) with elimination of secondary pollutants, such as NO_x, CO, polyaromatic hydrocarbons, dioxins, etc. This is achieved by the use of highly active catalysts in a fluidized bed, which also allows the efficient removal and possible use of reaction heat. This environmentally safe technology was successfully tested in pilot and industrial plants upon combustion of various fuels and wastes [37–39] including spent scintillation fluids [39].

The project for development of the technology of fluidized bed catalytic destruction of mixed organic waste containing radionuclides was carried out in 1994–1998 by the BIC in cooperation with the Novosibirsk Plant of Chemical Concentrates (PCC) and other former nuclear weapons materials processing plants in Tomsk-7 Krasnoyarsk-26, -45 and Angarsk, and with LLNL as the US collaborator under the ISTC project No. 110. The process is based on total oxidation of waste organic components in a fluidized catalyst bed and transition of radionuclides to a compact solid phase for further processing or disposal [20–23].

In the development of this technology the following tasks were accomplished:

- Selection of a suitable active, thermally stable and mechanically strong catalysts;
- Study of the combustion efficiency for waste organic components and exhaust gas composition after catalytic reactor and off-gas treatment units;
- The composition and size of the particulates after the catalytic reactor and after off-gas treatment units;
- The fate of radionuclides;
- The influence of accumulation of radionuclides in the catalyst on its properties;
- Optimization of parameters of processes of catalytic combustion and off-gas treatment.

The final goal of this work is the demonstration of the technology in the prototype industrial plant at Novosibirsk Plant of Chemical Concentrates where fuel rods are produced. The plant is intended for the treatment of the annual amount of 50 t of liquid organic mixed wastes represented mainly by lubricants and vacuum pump oils contaminated by uranium isotopes.

For study of mixed organic waste catalytic destruction two pilot installations of 1 kg/h capacity were designed, manufactured and assembled.

The first installation was specially designed for the study of processes of catalytic combustion of simulated waste and processes of exhaust gas purification from particles of surrogate non-radioactive metal oxides and acid gases. It includes a fluidized bed catalytic reactor, cyclone, jet scrubber, two absorber–condensers and an aerosol filter (Figs. 1 and 2). The installation operates as follows. The compressed air is supplied to the reactor by compressor (12) in the quantity sufficient for fluidization and total waste combustion at the bed temperature 600–780°C. The wastes from the tank (10) are fed into the reactor by the pump (8) and sprayed in the catalyst bed through the nozzle. The heat of the reaction of waste oxidation is removed by the heat exchanger (2) immersed in the catalyst bed, and the exhaust gas temperature can be decreased to 250–300°C. The exhaust gas from the reactor enters the cyclone (3) where large-sized particles are separated and the gas temperature is decreased to 200–250°C. Traces of unburned organics and CO are removed in the catalytic converter (4) containing a monolithic honeycomb oxidation catalyst. Then the gas passes through a foam jet scrubber (5) which acts both as a gas and particulates trap, and as a regenerative heat exchanger. It removes medium-sized particles (>5 μm) and the major part of acidic admixtures, such as oxides of sulfur and phosphorous. The temperature of the gas decreases to 70–90°C. The feed of scrubbing solution is effected by the pump 9/1. After the jet-scrubber, the gas saturated with water vapor enters the absorber–condensers (6) where, in a condensational regime, their purification from low-sized particles takes place with final removal of trace amounts of acid gases and gas cooling to 20–25°C. The scrubbing solutions are fed to the nozzles of the absorber–condensers by pumps 9/2, 9/3. Final purification of the gas is carried out in the aerosol filter (7). To exclude the condensation of water on the filter, the gas is heated to 35–40°C by the water heat exchanger (13) using the heat generated from the combustion of wastes.

The second installation was constructed at PCC for the experiments with radioactive wastes of the plant to study catalyst performance in destruction of real radioactive materials (Fig. 3). It includes a catalytic reactor of 120 mm diameter and a cyclone, systems for supply of air and wastes and a system of measurement and control, and does not have its own off-gas treatment equipment. The exhaust gas from this installation is directed to the centralized off-gas treatment system of the plant.

At BIC, efficient catalysts for application in fluidized bed combustion of organic wastes were developed and batches of catalyst were prepared for testing in the pilot installations.

In a fluidized bed reactor, the catalyst is subjected to the following combined severe effects: mechanical shocks and attrition; high temperature; chemical action of stoichiometric fuel/air mixtures; poisoning effects of sulfur, alkaline metals and other elements for the case of combustion of crude fuels and organic wastes.

Therefore the requirements of high thermal stability, conservation of sufficient activity during long operation in media with low oxygen concentration; resistance to catalytic poisons; high mechanical strength, and spherical form to reduce attrition are imposed on these catalysts.

One of the most important problems encountered in the use of fluidized bed combustion is catalyst attrition. To solve this problem, special mechanically strong (crushing strength up to 50 MPa) catalysts were developed [40]. The catalysts are prepared by supporting oxides of Fe, Cr, Mg, Cu and other metals on strong spherical γ-alumina beads with a high specific surface area. Spherical form results in less abrasion of catalyst particles in fluidized bed operation. The impregnation technique used for preparation of the catalysts provides uniform distribution of an active component throughout the beads and ensures that catalyst attrition has no effect on catalytic activity.

The study of catalyst deactivation and deterioration during operation in a fluidized bed [30,41–44] led to formulation of the principles for the catalyst selection:

- An active component should not have a mineralizing effect on the support;
- Catalysts should retain high mechanical strength after thermal treatment at 700–1200°C;
- The interaction of an active component with a support should lead to granule strengthening;
- The products of the interaction of an active component with a support should have a sufficient

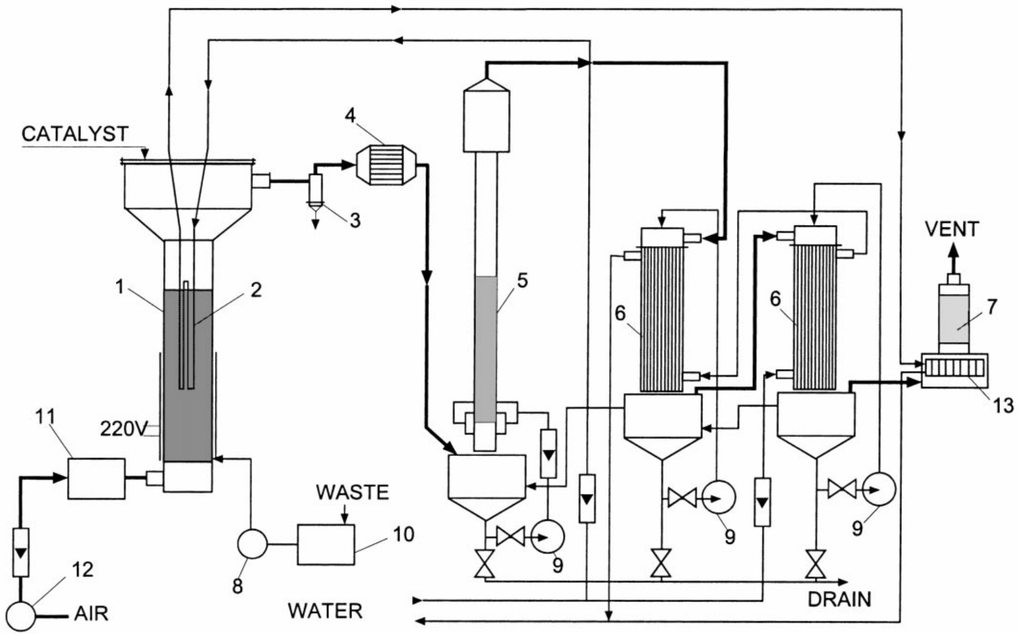


Fig. 1. Schematic diagram of the pilot installation No. 1: 1 – fluidized bed reactor, 2 – heat exchanger, 3 – cyclone, 4 – CO catalytic converter, 5 – jet scrubber, 6 – absorber–condensers, 7 – aerosol filter, 8 – waste pump, 9 – water pumps, 10 – tank with wastes, 11 – electric heater, 12 – compressor, 13 – heat exchanger.

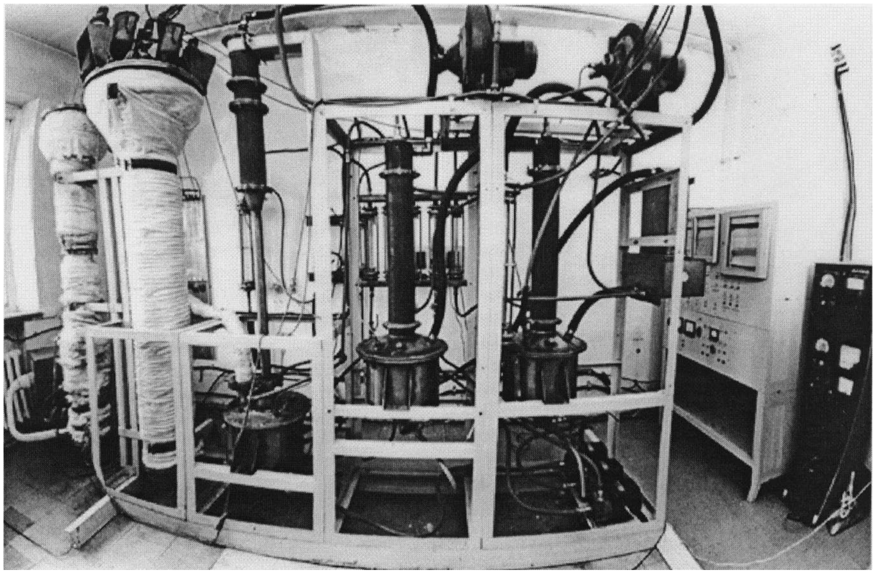


Fig. 2. Photograph of pilot plant No. 1.

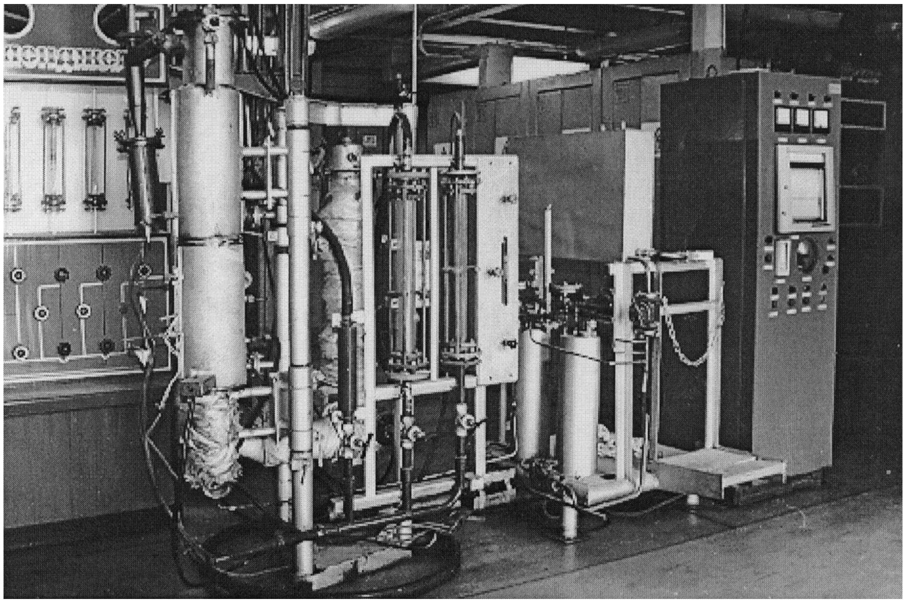


Fig. 3. Photograph of the pilot installation No. 2.

catalytic activity for the complete oxidation of organic compounds.

On the basis of these principles and the results of the complex study of the interactions of oxide compounds of transition metals with various alumina supports, a series of novel combustion catalysts with high mechanical and thermal durability, different in particular catalytic properties were developed [40,45–50].

The catalysts that have the most optimum operational properties are those based on magnesium chromite: IC-12-72 (20% $MgCr_2O_4/\gamma\text{-}Al_2O_3$) and IC-12-73 (20% $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$) (Table 2). These catalysts retain high activity during long operation at 600–780°C, are resistant to sulfur poisoning, and have high mechanical strength providing low catalyst attrition — less than 0.5% per day.

The experiments on catalytic combustion of the mixed waste organic components were carried out in both of the pilot installations with a variety of oils and solvents supplied from nuclear materials plants participating in the project. The experiments showed that in all cases a high efficiency of organics conversion is achieved. The analysis of the total organic content performed with chromatographic FID detector showed the content of organic compounds to be below 10 mg/m^3. The typical composition of the exhaust gas after the catalytic fluidized bed reactor is: combustion products CO_2 and H_2O, small amounts of CO (30–400 ppm), NO_x (10–60 ppm), SO_2 (3–30 ppm), and particulate matter (50–200 mg/m^3) formed from the ash residue of wastes and due to catalyst attrition.

In order to remove from the exhaust gas of the fluidized bed catalytic reactor traces of organics and CO, it was proposed to install a platinum monolithic catalyst (CO converter) after the cyclone. Platinum containing catalysts on monolithic honeycomb aluminosilica supports were specially designed to remove CO from dust loaded gases [51]. The catalyst is a rectangular monolith (72 mm × 72 mm × 75 mm) with a large number of parallel rectangular channels (2 mm × 2 mm) separated by thin walls on which the active component is supported. The CO converter was installed between the cyclone and the jet scrubber.

The concentration of CO in the flue gas upon catalytic combustion of oils was 50−400 ppm for the catalyst $MgCr_2O_4/\gamma\text{-}Al_2O_3$ and 30–40 ppm for the catalyst $Cu\text{–}MgCr_2O_4/\gamma\text{-}Al_2O_3$. CO converter provides CO removal over 95%, thus decreasing CO concentration below 16 ppm — the maximum allowable value in air according to Russian Standard for production areas.

The various regimes of the processes of catalytic combustion and off gas purification in the pilot in-

Table 2
Characteristics of catalysts used in experiments

No.	Characteristic	Unit	IC-12-72	IC-12-73
1	Composition		$MgCr_2O_4/\gamma\text{-}Al_2O_3$	$Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$
2	Content of main fraction (1.4–2.0 mm)	%	95	94
3	Bulk density	g/cm^3	1.04	1.10
4	*Crushing strength*	MPa		
	average		45.2	48.9
	minimum		25.9	22.5
5	Content of active component	%	Cr_2O_3 – 15.8, MgO – 4.2	Cr_2O_3 – 17.0, MgO – 3.6, CuO – 1.7
6	BET area	m^2/g	119	131
7	Activity in CO oxidation — temperature of 50% CO conversion	°C	354	238
8	Activity in butane oxidation — reaction rate at 400°C and steady-state concentration of butane 0.2 vol%	cm^3/g s × 10^{-2}	2.34	2.51

Table 3
Results of analysis (ppm) of CO and nitrogen oxides in off-gas gases composition upon catalytic combustion of oil sludge

Temperature in catalytic reactor	Units where gas probes are taken	CO	NO	NO_2
780°C	Cyclone	24	58	1
	CO converter	0	54	4
	Jet scrubber	0	55	4
	Absorber–condenser 1	0	56	1
	Absorber–condenser 2	0	49	0
710°C	Cyclone	98	18	1
	CO converter	0	17	4
	Jet scrubber	0	17	3
	Absorber–condenser 1	0	16	1
	Absorber–condenser 2	0	16	0

stallations were examined. Under optimum regimes, the concentration of NO_x was 5–30 ppm, that of CO was 15 ppm, and SO_2 1–10 ppm, and concentrations of particulate were less than 1 mg/m^3. Table 3 shows how harmful emissions can be controlled by catalytic incineration of oil sludge. The three-fold decrease of NO_x emission can be attained by the decrease of temperature from 790 to 710°C. The resulting increase of CO concentration after the fluidized bed reactor is not a problem, as CO is almost totally oxidized in CO converter.

The particulates in the gas stream after the fluidized bed catalytic reactor are formed from inorganic admixtures (ash) of the wastes and also from the catalyst attrition. The values of dust concentration in the gas stream are usually in the range of 50–200 mg/m^3. The data on dust concentration and its removal by various gas cleaning units are presented in Table 4. The results show that gas cleaning units efficiently remove particulates from the gas stream. After the absorber–condensers, the dust is practically absent in the gas within the sensitivity of the analytical method used ($<$1 mg/m^3).

The experiments in pilot installations revealed a phenomenon of radionuclide accumulation in the catalyst. A series of experiments were carried out with model wastes containing additions of W and Th compounds simulating admixtures of uranium in real wastes. First, the catalytic combustion of an individual waste component (lubricating oil) was studied, then the oil was doped with sodium tungstate to W concentrations of 112 and 1673 mg/l, or with thorium nitrate to Th concentrations of 40 and 200 mg/l, and the resulting suspension was fed into the fluidized bed reactor.

The analysis of the results obtained in the study of catalytic combustion of simulated waste showed gradual accumulation of inorganic admixtures in the catalyst granules, in the catalyst dust captured by the cyclone and the scrubbing liquids in the gas cleaning units (Fig. 4), the major part (over 50%) of inorganic admixtures being retained in catalyst granules. The gas cleaning units efficiently remove the remaining part of the W or Th from the gas stream. The distribution of the metal oxide over gas cleaning units show that over

Table 4
Results of the study of dust removal by gas cleaning units upon catalytic combustion of industrial oil I-50A

No.	Apparatus	Dust concentration ((mg/m^3), after apparatus)	Dust removal (%, of total)	Size of removed particles (μm)	Dust removal (%, from initial concentration)
1	Reactor	165			–
2	Cyclone	36.4	77.9	28–160	77.93
3	Jet scrubber	8.5	16.9	3–28	94.85
4	Absorber–condenser 1	2.2	3.8	<3	98.67
5	Absorber–condenser 2	<1	≥0.9	<3	>99.5

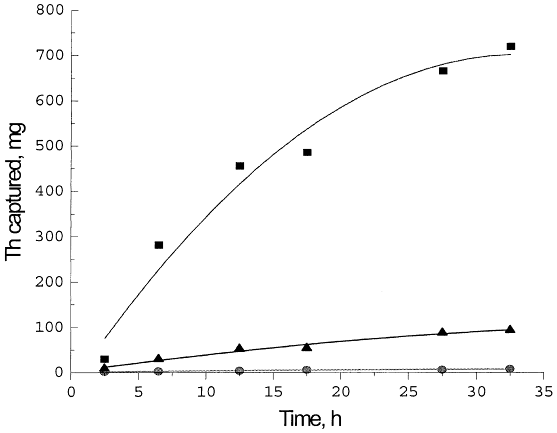


Fig. 4. Accumulation of Th in catalyst granules (■), gas cleaning units (▲) and catalyst dust in cyclone (·).

80–90% of the metal is removed from the gas stream in the jet scrubber and the remaining part is captured in the absorber–condensers.

The distribution of the metal from waste in catalyst granules was studied by the X-ray microprobe technique. The granule, held in epoxy resin, was cut stepwise and each section was scanned by the X-ray microprobe analyzer providing data on the local concentration of the metal. The results obtained (Fig. 5) show that the metals are mostly concentrated at the outside surface of the catalyst beads. This accounts for larger concentrations of the metals in the catalyst dust captured by the cyclone, formed as a result of catalyst attrition.

The main catalyst characteristics: mechanical strength, specific surface area and activity during experiments were maintained at the level sufficient for stable and efficient waste catalytic destruction.

The accumulation of U in catalyst granules upon catalytic treatment of spent oils and extractants of fuel rods production with uranium content 120 and 10 g/l, respectively was studied in the pilot installation at PCC. The experiments confirmed high efficiency of the proposed method for the treatment of the industrial mixed wastes containing uranium. The results show that the ratio between uranium captured in the catalyst bed and removed from the bed by the flow of the reaction products is dependent on the type of the wastes and uranium content, and up to 70% of uranium is retained in catalyst granules. This allows for reduction of the load on the off-gas treatment system and an increase of its efficiency. The radionuclides can be recovered from the spent catalyst by conventional methods, e.g. by dissolving of the spent catalyst in nitric acid and the subsequent extraction by tributyl phosphate.

The experimental results obtained in pilot-scale experiments showed the technology of fluidized bed

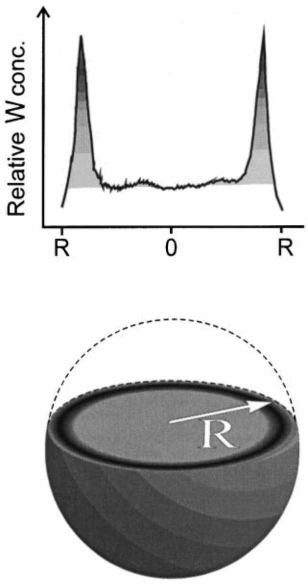
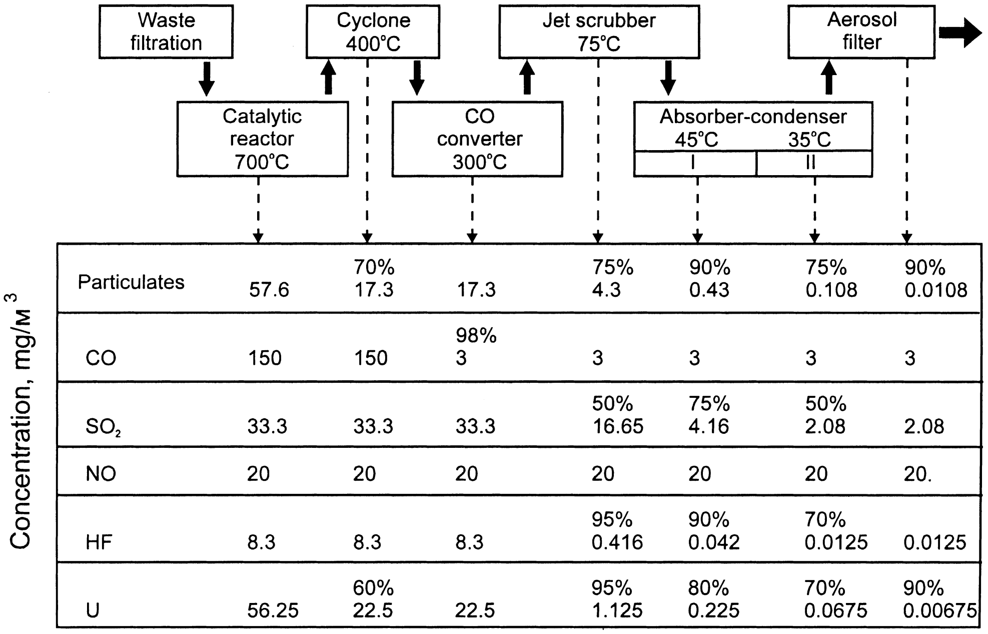


Fig. 5. Distribution of W over catalyst granule.



Particulates	57.6	70% 17.3	17.3	75% 4.3	90% 0.43	75% 0.108	90% 0.0108
CO	150	150	98% 3	3	3	3	3
SO_2	33.3	33.3	33.3	50% 16.65	75% 4.16	50% 2.08	2.08
NO	20	20	20	20	20	20	20.
HF	8.3	8.3	8.3	95% 0.416	90% 0.042	70% 0.0125	0.0125
U	56.25	60% 22.5	22.5	95% 1.125	80% 0.225	70% 0.0675	90% 0.00675

Fig. 6. Prototype demonstration plant design and emission characteristics.

catalytic combustion to be efficient for environmentally safe treatment of liquid organic wastes containing radionuclides. Based on these studies, a technological scheme and design documentation of the prototype demonstration plant for treatment of PCC mixed liquid organic wastes formed in fuel rods production with a capacity of 50 t/year were prepared. The block diagram of the demonstration plant with expected emission characteristics is given in Fig. 6, and the photograph of the catalytic fluidized bed reactor of the plant is shown in Fig. 7. At present the fabrication of all apparatuses of the plant is finished, the assembly of the plant is completed and the tests of the plant are planned at the end of 1998. The plant is intended to solve one of the urgent environmental problems of Novosibirsk Region by reducing the volume of mixed waste by 100 times and transition it to less hazardous forms, which are safely disposed by existing technologies.

At the present stage the technology developed was tested only with liquid mixed waste, but it can be also applied to many types of solid mixed waste. This application requires only modification of waste preparation and waste feeding units.

The scientific and technical results obtained provided a reliable basis for future evolution of the technology. Since 1998 a new program for development of the technology for destruction of mixed organic radioactive wastes of radiochemical and chemical–metallurgical plants at Tomsk-7, which contain enriched uranium (up to 90%), isotopes of plutonium (^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) and fission products, is started. In this project different approaches will be examined: both direct waste destruction in a catalyst fluidized bed and combined processes, when the waste is initially pyrolysed or processes in molten salt bath and then the resulting gas mixture is oxidized over a catalyst.

3. Oxidation of mixed organic waste in molten catalysts

In the conventional molten salt oxidation (MSO) process, a solid, liquid or gaseous combustible waste is injected with an excess of air or oxygen into a pool of molten salt, typically, sodium carbonate, alone or mixed with sulfates or other salts. An operating temperature is kept constant between 900 and 1000°C [52,53]. Off gases are cooled and filtered to remove particulate matter. As all potential acids in off-gases

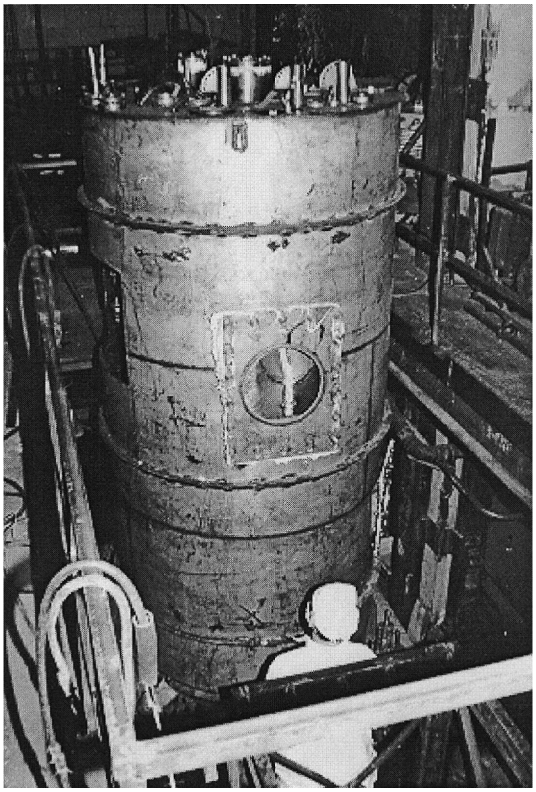


Fig. 7. Catalytic fluidized bed reactor of the demonstration plant.

are adsorbed by the alkaline melt, acid scrubber units producing large amounts of wastewater are not necessary, which is a rather attractive feature of the MSO method.

In the USA, the MSO process is considered to be a promising technology for mixed waste destruction. At Lawrence Livermore National Laboratory, an integrated pilot-scale MSO treatment system has been designed and constructed, in which tests and demonstrations are presently being performed under controlled conditions. A primary purpose of these demonstrations is to identify the most suitable waste streams and waste types for MSO treatment [54].

It is important to note that total destruction of organic compounds in molten sodium carbonate occurs at a rather high temperature ca. 950°C, and it is known that molten salts, in particular carbonates, are very corrosive at these temperatures [55]. Under these conditions NO_x formation takes place, especially if nitrogen containing compounds are present in the waste treated.

As such, we have initiated a research program to improve the performance of MSO process and decrease operating temperatures using melts with catalytic properties. An alternative catalytic technology for organic waste treatment by MSO in catalytically active molten salts was studied with model compounds: C_3H_8, CO, CCl_4, chlorobenzene, etc. in alkaline or carbonate melts doped with transition metal oxides and the catalytically active K_2O–V_2O_5 system. [56,57].

The following systems were studied: NaOH–KOH; LiCl–KCl, Li_2SO_4–Na_2SO_4, Li_2CO_3–K_2CO_3; carbonates doped with transition metal oxides (Fe_2O_3, Cr_2O_3, Co_3O_4, MnO_2), and the catalytically active K_2O–V_2O_5 system (pure and doped with CuO). The effects of melt composition, oxygen concentration, space velocity and temperature on destruction efficiency were examined. The experiments were carried out in a bubble type stainless steel reactor, the analysis of reaction mixtures was performed by gas chromatography.

Comparison of oxidation of CO and methane in molten sulfates, chlorides and carbonates showed that the oxidation in both sulfate and chloride melts is accompanied by formation of products of pyrolysis and partial oxidation. In the melt and on the reactor's walls soot was formed; and in the reaction products CO and H_2 were detected. In carbonate melts only products of complete oxidation were observed, and the next series of experiments were performed with carbonate melts — both pure and doped with transition metal oxides.

Oxidation of CO in Li_2CO_3–K_2CO_3 was studied using the salt composition with 65 mol% of Li_2CO_3 (50 wt.%), close to the eutectic. The temperature of the crystallization of this melt (515°C) is sufficiently low. This permits to study the process in a wide temperature range. The data on CO oxidation in the melt Li_2CO_3–K_2CO_3 show that a substantial CO conversion occurs in the range of 700–850°C, with the temperature of half conversion ($T_{50\%}$) being 780°C. A decrease of $T_{50\%}$ — by 15–30°C was observed for CO oxidation in doped carbonates. Therefore, the addition of 5 wt.% of metal oxides to the carbonate melt increases its activity in CO oxidation.

The fusion of alkaline metal carbonates with V_2O_5 is accompanied with CO_2 evolution and the formation of the catalytically active molten system K_2O–V_2O_5. The maximum activity was found for the molten

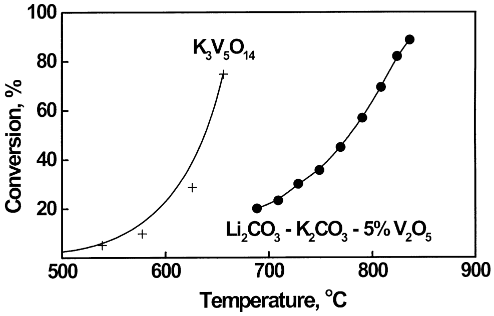


Fig. 8. Conversion of CO (1 vol% in air) vs. temperature in Li_2CO_3–K_2CO_3 + 5 wt.% of V_2O_5 and $K_3V_5O_{14}$.

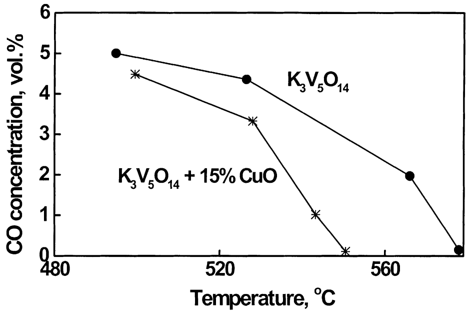


Fig. 9. Dependence of CO concentration on temperature upon C_6H_5Cl oxidation (10 vol% in O_2) in the melts: $K_3V_5O_{14}$ and $K_3V_5O_{14}$ + CuO, V = 80 h^{-1}.

catalyst of the $K_3V_5O_{14}$ composition with $T_{50\%}$ decreased from 760 to 640°C. (Fig. 8)

The introduction into the K_2O–V_2O_5 system of additions of transition metal oxides, in particular cupric oxide, further increases the activity of the melt in oxidative reactions. We observed a substantial decrease of $T_{50\%}$ by over 100°C for CO oxidation in molten $K_3V_5O_{14}$ when this melt was doped with 2.3 wt.% of CuO. This effect is explained by the formation of non-stoichiometric compounds, so-called bronzes that provide a high rate of oxygen diffusion in the crystal lattice [56].

The oxidation of chlorobenzene (CB) — 0.1 vol% in air in carbonate systems is characterized by the value of $T_{50\%}$ = 700°C. The addition of 5 wt.% of oxides of Cr, Mn and Fe has no marked effect on this value. Larger amounts (10 wt.%) of Cr_2O_3 and MnO_2 added to the melt or the addition of 5 wt.% of Co_3O_4 result in a decrease of the oxidation temperature by 40–70°C.

When chlorobenzene at a higher concentration of 3 vol% — was oxidized by oxygen in a NaOH–KOH melt, the formation of soot on the reactor's walls and the bubbler indicates pyrolysis of chlorobenzene and the activity of the melt decreased with time due to formation of chlorides and resulting decrease of concentration of metal hydroxides. When 10 wt.% of V_2O_5 is added to the alkaline melt, the decrease of the activity with time is less pronounced. But in this case some amounts of soot are also formed. A further increase of the content of V_2O_5 in the melt (as in the case of carbonates) results in the transition to the catalytically active K_2O–V_2O_5 system. Total conversion of CB in the $K_3V_5O_{14}$ melt to the reaction products: CO_2, CO, H_2O and HCl occurs at rather low temperatures — 500–600°C, i.e. by 400°C less than in the baseline technology of MSO in sodium carbonate melt.

The amount of CO in the exhaust gas decreases with temperature (Fig. 9). It was shown that the addition of 15 mol% of CuO to the $K_3V_5O_{14}$ melt improves considerably its activity and selectivity in CB oxidation to CO_2. For example, at 80 h^{-1}, the temperature at which the selectivity to CO_2 reaches 100% is 580°C for pure $K_3V_5O_{14}$ and 550°C for the catalyst modified with CuO (Fig. 9).

Thus, waste oxidation technology in catalytically active melts appears to be promising for the destruction of hazardous organic wastes, including mixed organic wastes.

In comparison with conventional thermal MSO, the application of catalytically active melts for treatment of mixed organic waste increases the destruction efficiency and lowers operational temperatures by hundreds of degrees, leading to the following benefits:

- VOC formation is suppressed;
- NO_x emission is minimized;
- Corrosion of reactor walls is decreased.

For special application of treatment of mixed wastes from Pu production, the combination of a catalytic MSO process with alkaline melts eliminates the need for extensive off-gas wet scrubbing because the major part of radionuclides and toxic acid gases, such as HCl, HF, SO_2 are absorbed in the melt.

4. Abatement of nitrogen oxides in gas streams

Nitrogen oxides are the most common pollutants of gas streams both in processes of Pu and U production and waste processing in nuclear industry. They are formed in flame incinerators, in plasma arc waste treatment installations, in glass melters used for a waste vitrification process — practically in all waste treatment processes carried out in a flame or at high temperature [8]. There are two main sources of NO_x — oxidation of atmospheric air via the Zeldovich mechanism (thermal NO_x), and oxidation of nitrogen-bearing compounds in the waste or fuel — so-called fuel NO_x. Widespread use of nitric acid in the nuclear industry for processing of U_3O_8 concentrate, reprocessing of fuel assemblies, and in the Purex process for Pu production leads to large amounts of nitrites and nitrates in nuclear waste. This results in a very high concentration of NO_x in the off-gas of waste thermal processing, exceeding 10 000 ppm.

Several approaches are known for the abatement of nitrogen oxide emissions from stationary or mobile sources, but the catalytic approach is the most efficient to meet current and future requirements.

SCR with ammonia and SCR with hydrocarbons are most efficient for NO_x catalytic removal in the presence of oxygen.

The former process is better studied and implemented on the industrial scale. The latter process looks more promising for the future because it avoids the problems associated with transport and handling of large amounts of ammonia, and the secondary pollution resulting from ammonia slip, but it is still at the research and development stage to design catalysts with sufficient stability in practical conditions.

At present in the Nuclear Industry for abatement of NO_x in gas streams, SCR with ammonia is commonly used because this process has been proven efficient at an industrial scale and is widely used in Japan and Europe for removal of NO_x from flue gas at power plants [6–8].

Commercial catalysts currently used to reduce NO_x from power plant flue gas proved their efficiency at NO_x concentrations around 1000 ppm. They consist primarily of vanadium pentoxide, titanium dioxide, molybdenum and tungsten oxides [6]. The high content of vanadium, molybdenum and other toxic metals in these catalysts prevents the disposal of the spent catalysts in US landfills. Currently the US Environmental Protection Agency has prescribed the toxicity characteristic leaching procedure (TCLP) [58,59] as the test for determining whether a waste (in this case spent catalyst) is to be classified chemically toxic, which will prohibit its land disposal. To satisfy TCLP tests total threshold limit concentrations of vanadium in $DeNO_x$ catalysts should not exceed 2400 mg/kg.

In mixed waste thermal treatment off-gas systems, it is difficult to determine how much ammonia must be introduced into the off-gas because the amount of NO_x in the stream can change appreciably in a short time due to variations in the waste being treated. Thus, the key requirement on an effective SCR process is that the catalyst be capable of converting (destroying) excess ammonia.

Thus, there are three main requirements for an efficient ammonia SCR catalyst. First, it should be capable of treating gases with NO_x concentration up to 10 000 ppm and be at least as effective as existing catalysts; second, that it be land-disposable (environmentally benign); and, third, that it be capable of converting excess ammonia to nitrogen.

Several types of honeycomb monolithic SCR catalysts have been designed and prepared with the aim to develop an efficient $DeNO_x$ catalyst for operation at NO_x concentration up to 10 000 ppm and to achieve environmentally benign quality while meeting the above noted requirements (Table 5). The catalysts were prepared in the form of rectangular monoliths with a cross-section of 75 mm × 75 mm, length 150 mm, channel size 4.2 mm and wall thickness 0.8 mm.

Three methods were used for the preparation of the catalysts:

1. Washcoating of ceramic monolithic supports by suspension containing active components;
2. Impregnation of monolithic supports by solutions containing salts of active components;
3. Extrusion of masses containing a mixture of active components.

The United States Department of Energy (DOE) has sponsored a series of pilot-scale plasma incineration tests at the MSE facility in Butte, MT, during FY97 and FY98 under the controlled emission demonstration (CED) program [8]. One of the objectives of the test series was to evaluate the performance of new Russian $DeNO_x$ catalysts developed by BIC for removal of high concentrations of NO_x from the off-gas generated by the plasma arc processor furnace.

Prepared catalysts were characterized at BIC and tested at LLNL (IC-44/1-700) and at the MSE facility

Table 5
Composition of $DeNO_x$ catalysts prepared for testing in NO_x abatement from off-gas of the plasma arc process

Catalyst	Preparation method	Chemical composition of support	Composition of washcoating	Active component (wt.%)
IC-44	Impregnation	Zn–Cr–Fe–O	CuO	CuO – 0.20
IC-45	Washcoating	Al_2O_3–SiO_2	Al_2O_3 (20%) + TiO_2–V_2O_5 (80%)	TiO_2 – 2.47, V_2O_5 – 0.13
IC-46	Washcoating	Zn–Cr–Fe–O	Al_2O_3 (20%) + TiO_2–V_2O_5 (80%)	TiO_2 – 2.6, V_2O_5 – 0.13
IC-47	Mixing (bulk)	Cu–V–Ti–W–O	–	CuO – 0.31, V_2O_5 – 0.13, WO_3 – 10.0, TiO_2 balance

in Butte, MT, under the controlled emissions program against a conventional industrial catalyst at various temperatures (300–400°C), various ratios of NH_3/NO_x (0.8/1–1.5/1) and high inlet NO_x concentrations — up to 4000 ppm.

The Plasma Arc Centrifugal Treatment (PACT-6) system was equipped with a transferred-mode 500 kW torch and was operated under oxidizing conditions (10–15% oxygen at the stack). Off-gas components from the PACT-6 primary chamber consist of nitrogen oxides NO_x, particulate material, products of incomplete combustion, high-vapor-pressure metals, and volatile chlorinated compounds as determined by the waste material being processed.

The best results on the IC-44/1-700 catalyst designated as a baseline sample were obtained at a temperature 303°C (the first stage of the catalytic bed), 1.5 : 1 $NH_3 : NO_x$ ratio, and NO_x concentrations of approximately 2650 ppm (2526 ppm of NO). The removal efficiency of NO was 81%, NO_2 - 94%, and NH_3 - 74%. Correspondingly, the baseline industrial catalyst demonstrated 90, 92 and 64% for the same nitrogen compounds. TCLP analysis was performed on one of the removed catalyst blocks after the $DeNO_x$ test series and it failed to pass the TCLP analysis for one metal, chromium. The IC-45 catalyst formulation is environmentally benign as compared to the formulations of the IC-44/I-700, but the performance of this catalyst was found to be inferior with respect to the baseline IC-44/I-700 and baseline industrial catalyst.

The best performance was found for the IC-47 catalyst at a temperature 372°C, 1 : 1 $NH_3 : NO_x$ ratio, and NO_x concentration of approximately 3500 ppm (3217 ppm of NO). The removal efficiency of NO was 95.9%, NO_2 - 96.5%, and NH_3 - 88.5%. Correspondingly, the baseline industrial catalyst demonstrated 91.9, 99.3 and 86.3% for the same nitrogen compounds. TCLP analysis was performed on one of the spare IC-47 catalyst blocks that was not installed in the $DeNO_x$ unit. This IC-47 catalyst passed the TCLP analysis. The results of catalyst testing in SCR of NO_x are given in Fig. 10.

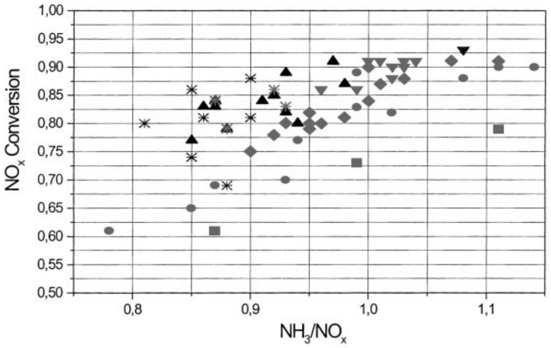


Fig. 10. NO_x conversion vs. NH_3/NO_x for the catalysts studied: (●) baseline industrial catalyst-1, T = 300°C, (◆) baseline industrial catalyst-2, T = 300°C, (■) Russian baseline IC-44/I-700 catalyst, T = 300°C, (▲) Russian catalyst IC-47, T = 325°C (✳) Russian catalyst IC-47, T = 350°C and (▼) Russian catalyst IC-47, T = 375°C.

Thus, all prepared catalysts were shown to be active in SCR of NO_x by ammonia and the IC-47 demonstrated both the highest performance in removal of NO_x and NH_3 (comparable with and exceeding the performance of a commercial catalyst), and also low toxicity in leaching procedure analysis, proving that this catalyst is environmentally benign for the landfill disposal.

As was mentioned above, the SCR of NO_x with hydrocarbons (HC-SCR) is a more convenient and safe process, because it avoids the problems of transport and handling of large amounts of ammonia, and the secondary pollution resulting from ammonia slip. In the literature there are many publications on this subject, which started since Iwamoto et al [60,61] and Held [62] reported in 1991 a significant activity of copper ion-exchanged zeolites (Cu-ZSM-5) for this reaction under oxidizing conditions. Various other metal-exchanged zeolites such as Ga-ZSM-5 [63,64], Co-ZSM-5 [65–67], Ce-ZSM-5 [68–71], etc. have been found to be active in the selective NO reduction by hydrocarbons in oxygen-rich atmospheres. Their activity, however, depends considerably on the hydrocarbon used and on the experimental conditions [72,73], unlike copper-zeolites which show a high activity in a wider range of reaction conditions and with more hydrocarbons. Other types of catalysts: metal oxides [74] and noble metals [75–77] can be also effective under certain conditions, but on the whole their performance is inferior to the ion-exchanged zeolites.

Most of the studies performed on HC-SCR concerned powdered zeolite catalysts, although the commercial HC-SCR catalyst will be a metal or ceramic monolith because of pressure drop and space constraints. However, very few papers are devoted to preparation of monolithic catalysts required for practical application. As an example, Co-ZSM-5 used for CH_4-SCR under simulated flue gas conditions is the first comprehensive attempt to study these catalysts in a monolithic form [78]. It showed similar activity trends to those observed for the powder catalyst. In [79], Cu-exchanged ZSM-5 was washcoated on a honeycomb substrate. Metal-exchanged zeolite catalysts of new type — ZSM-5 or mordenite directly grown on a metal gauze support and subsequently exchanged with metal ions were studied in [70] and proved to be efficient catalysts.

Recently in BIC a series of granulated and monolithic metal oxide and ion-exchanged zeolite catalysts were developed, and the catalyst activity was studied in the HC-SCR reaction with propane as a reducing agent.

The oxide catalysts were prepared by supporting Co and Cu oxides on alumina ring and spherical supports both in pure form and modified with the additions of La, Ce and Zr oxides. The influence of the calcination temperature, type of modifying elements, content of the active component and type of the salt containing the cation of the active component were studied. These catalysts were shown to have rather low activity — with maximum 40% of NO_x conversion found for the Co catalyst at 550°C.

The ion-exchanged zeolite catalysts were prepared as washcoated monoliths on ceramic cordierite or an aluminosilicate matrix. For the preparation of washcoated monolithic honeycomb supports, a suspension of sol-aluminium hydroxide with a pseudoboemite structure was used. This sol, formed during the reaction between the hydroxide and nitric acid, serves both as a binder and as a source of γ-Al_2O_3 after calcination. A zeolite powder (particle size $\approx 30\,\mu m$) was introduced into the sol. The influence of the following parameters on the formation of the washcoated support were studied: the concentration of anhydrous alumina in the sol; the amount of HNO_3 and the amount of zeolite introduced; duration of the dipping into the aqueous solution of metal salt, the number of dippings, drying and calcination time.

The washcoated supports were used for the preparation of washcoated catalysts by ion-exchange from aqueous metal salt solutions. The concentration of metal cation was varied and depended on the ion-exchange time (for Cu-ZSM-5) and the number of dippings (for Co-ZSM-5). Ce was introduced from a Ce nitrate solution with the concentration of 0.01 and 0.1 M by the ion-exchange technique. A (Cu + Ce) catalyst was prepared from a mixed solution containing Cu acetate and Ce nitrate. Cu/Ce-ZSM-5 and Ce/Cu-ZSM-5 catalysts were prepared from individual solutions of Ce and Cu salts at the variation of the sequence of ion-exchange procedure.

The catalytic activity of the catalysts prepared was determined in the SCR of NO by C_3H_8 and was characterized by the NO conversion to N_2. The study was carried out in a flow reactor in the temperature range 20–600°C and space velocity 21 000 and 42 000 h^{-1}. The space velocity was changed by the variation of the inlet gas mixture flow at a constant amount of catalyst – 4 cm^3. The inlet gas mixture had a constant composition: $NO = 300$ ppm; $C_3H_8 = 0.15$ vol%; $O_2 = 5$ vol%, balance N_2 and/or Ar.

The catalytic activity and its dependence on temperature for Cu-ZSM-5 and Co-ZSM-5 are similar. Their activities increase with the temperature increase from 55% at 450°C to 70% at 550°C. The doping with Ce as well as the sequence of its introduction had no noticeable effect on the activity. The decrease of space velocity to 21 000 h^{-1} results in a higher NO conversion — ca. 80% at a temperature 450–550°C.

In the process of vitrification of liquid mixed waste containing high concentrations of nitrates, their thermal decomposition can result in very high concentrations of NO_x — over 10 000 ppm. As currently envisioned, greater than 99% of NO_x must be removed from a gas stream that may contain up to 20 vol% of NO_x depending on the concentration of nitrates and the method of vitrification. In this case, SCR of NO_x with ammonia or hydrocarbons is not expected to provide the required efficiency. To solve this problem, a quite different approach was proposed by Pacific Northwest National Laboratory (USA). If the melter is preceded by a calciner (fluid bed, rotatory, or spray calciner) in which the mixed waste is first mixed with an organic reducing agent, e.g. a sugar solution, and then dried, calcined and simultaneously denitrated, it may be possible to gain two significant advantages: (1) avoid the formation of NO_x and (2) increase the throughput of the melter by feeding a dry powder and avoiding the vaporization of water in the melter.

One can represent the interaction of sugar with sodium nitrate by the following reactions, which reflect the formation of CO_2 and N_2 or CO and NH_3 depending on the amount of sugar present:

$$C_{12}H_{22}O_{11} + 9.6NaNO_3 = 4.8Na_2CO_3 + 7.2CO_2 + 11H_2O + 4.8N_2 \quad (1)$$

$$C_{12}H_{22}O_{11} + 3.43NaNO_3 1.71Na_2CO_3 + 10.29CO_2 + 5.86H_2O + 3.43NH_3 \quad (2)$$

To ensure total destruction of $NaNO_3$ one should take a certain excess of sugar over the stoichiometry of the reaction (1), therefore the formation of some amount of ammonia is unavoidable. This undesirable by-product can be removed most efficiently by catalytic selective oxidation to molecular nitrogen.

In BIC a large number (over 30 formulations) of catalysts were prepared and tested for the ammonia oxidation reaction in a flow recycle setup under the following conditions: initial gas mixture composition equals 800–900 ppm of NH_3, 2.5% of O_2, balance He; catalyst loading 0.4 g, catalyst particle size 0.4–1.0 mm, initial mixture flow rate 10.8 l/h. The activity and selectivity of catalysts prepared were characterized by reaction rates of formation of the products: N_2, NO and N_2O from ammonia at fixed temperatures of 250, 300 and 400°C [80]. The results for some of the most active and selective catalysts are given in Table 6. This study showed that the most active in ammonia oxidation to molecular nitrogen are vanadium–titanium and copper–titanium catalysts. They are promising for practical implementation for NH_3 removal from the vitrification process off-gas if produced as honeycomb monoliths.

Table 6
Activity of some catalysts developed for selective catalytic oxidation of ammonia

Catalyst	T (°C)	W (product formation), molec. NH_3/g s $\times 10^{-17}$		
		N_2	NO	N_2O
Fe–Bi–Mo	250	0.65	0	0
	300	0.76	0	0.06
	400	1.86	0.02	0.44
15% V_2O_5/TiO_2	250	0.13	0	0
	300	0.19	0	0
	400	0.94	0	0.12
4% CuO/TiO_2	250	0.25	0	0
	300	0.68	0	0
	400	1.65	0	0

5. Catalytic oxidation of hydrogen generated by radiolysis

A substantial part of radioactive wastes are high level aqueous solutions, containing transuranic elements ^{241}Am, ^{239}Pu, highly active fission products, such as ^{137}Cs, ^{90}Sr, ^{90}Y, ^{99}Tc, nitrate and nitrite ions, organic acids and other organic components. In the USA, a major part of such wastes are stored at Hanford in 177 tanks with a capacity of 1000–2000 m^3 each [11,12]. In Russia similar wastes are also accumulated in tanks, mainly in Krasnoyarsk-26, Tomsk-7 and Mayak. Storage of high level mixed liquid wastes is accompanied by the formation of explosive gas mixtures generated by radiolysis [9,10], containing on the average 39% H_2, 31% N_2O, and 30% N_2, which evolves with a rate of about 2 m^3 per day from a tank containing about 1000 m^3 of waste [11]. For prevention of explosion, the tanks are ventilated to reduce hydrogen concentrations below the lower explosive limit. But this approach may not be sufficient for complete safety of the tanks, because the formation of hydrogen proceeds mainly at the bottom of a sludge layer and the hydrogen comes out very irregularly in large bubbles erupting from the sediment. Thus, there may be moments when the local hydrogen concentration even after the dilution of the evolving gas with air exceeds the flammable value.

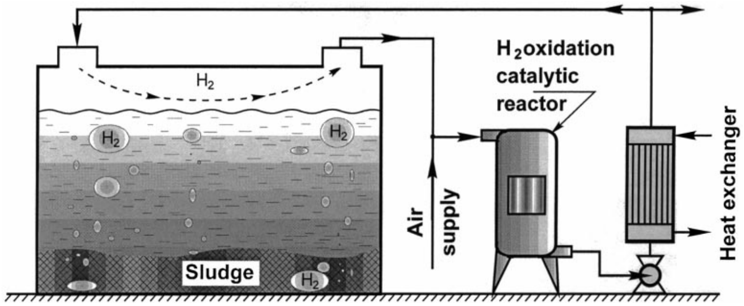


Fig. 11. Catalytic oxidation of hydrogen in the tank gas.

For instance, one of the Hanford tanks, 101-SY, was made famous by its violent releases of flammable gases [12]. The highly radioactive waste generated hydrogen, nitrogen, nitrous oxide and ammonia. The violent manner in which the gases would percolate, or 'burp' from the bottom of the tank had made the tank into one of Hanford's most serious safety concerns. To prevent the violent gas percolation, the Westinghouse Hanford Company has installed a mixing pump that allows gradual instead of instantaneous release of gases generated inside the tank. However, the fact that the tank still produces flammable gases necessitates reliable and continuous monitoring of the tank atmosphere and intensive ventilation to dilute the concentration of hydrogen below the explosive limits.

An efficient way to solve this problem and guarantee the tank safety is catalytic oxidation of hydrogen in the ventilation gas as shown in Fig. 11. The catalyst for this process should have a high activity at low temperature (150–200°C) and retain this activity in a humid gas stream.

There is a similar problem of hydrogen formation at nuclear heat supply plants. An explosive hydrogen–oxygen mixture is generated by radiolysis of cooling water in the active zone of the reactor. This mixture accumulates in steam condensers. There are technical difficulties preventing complete removal of this mixture from the condensers, so the best way to ensure the safety of the reactor will be to remove hydrogen completely by passing the steam containing radiolysis generated explosive H_2–O_2 mixtures through the oxidation catalyst. The conditions of catalyst operation in this case are extremely severe: high steam concentration at a temperature of 200–210°C and a high pressure of over 16–20 atm.

From the literature, it is known that conventional Pt catalysts supported on inorganic materials, such as alumina and silica, suffer significant deactivation at low temperatures as a result of the adsorption of water vapor by the supports. Consequently, such catalysts are usually operated at high temperatures (above 300°C) [81]. One way to use the high activity of Pt and avoid catalyst deactivation in humid gas streams at low temperatures is to utilize hydrophobic materials as a support. It was shown that Pt supported on fluorinated carbon and styrene divinylbenzene copolymer (SDB) considerably improved activity for oxidation of formaldehyde, CO [82,83], benzene [84] and toluene [85] in humid gas streams at temperatures below 150°C.

A series of Pt and Pd catalysts on granulated and monolithic supports for H_2 oxidation were prepared at BIC. They were tested for the H_2 oxidation reaction to estimate their activity and durability at temperatures of ca. 200°C in humid atmospheres (Table 7) [86].

The results showed that these catalysts have high initial activity, but some of them lose it rapidly due to removal of the active component from the support, catalyst deterioration, and condensation of water in small and medium sized pores. The experiments showed the possibility to reduce these effects by overheating the catalyst by 50°C above the temperature of the steam. In these conditions some of the catalysts with the optimum properties maintained their high activity — close to 100% of H_2 conversion, during relatively long operation — over 20 h. The best results were achieved with the catalyst on a hydrophobic supports, such as Pt or Pd supported on carbonized alumina or SDB. The work is being continued with the aim to develop an optimum composition of hydrophobic supports for

Table 7
Hydrogen conversion over different catalysts in dry and humid feeds[a]

Catalyst	Space velocity (h^{-1})	Catalyst loading (g)	X (% in dry feed)	X (% in humid feed, initial)	X (% in humid feed, in 3 h)
0.35% Pt/nichrome	2000	11.3	37	5	5
0.6% Pt/γ-Al_2O_3	27000	0.02	68	33	33
0.1% Pt/α-Al_2O_3 (monolithic)	2250	2.4	44	26	26
0.1% Pd/α-Al_2O_3 (monolithic)	9000	0.6	81	50	50
0.93% Pt/SDB	270000	0.02	60	60	57
5.1% Pt/SDB	270000	0.02	99	97	71

[a] Conditions: $T = 210°C$, $P = 19$ atm, H_2 concentration = 1 vol% in air, flow rate 5.4 l/h, humid feed — water vapor saturated at 210°C; SDB = styrene divinylbenzene copolymer.

noble metal catalysts providing both high activity and durability for thousands of hours.

6. Catalytic removal of VOCs formed in processes of soil remediation and groundwater cleaning

The remediation of former nuclear sites requires purification of soil and groundwater contaminated by cleaning solvents and degreasers entering the subsurface environment from accidentals spills, storage tanks and past disposal practices. One of the processes used commercially for cleaning these contaminated groundwater sites is by air (or steam) stripping of the VOCs followed by oxidation of these VOCs over a suitable catalyst [13–16]. The implementation of this technology meets with the following main problems:

- high humidity inhibiting catalytic oxidation [82–85],
- presence of chlorinated hydrocarbons causing catalyst deactivation [15,16] and formation of toxic chlorine-containing by-products, e.g. polychlorinated benzenes [87,88].

The solutions of these problems are correspondingly the following:

1. development of hydrophobic catalysts active in humid atmospheres [82–86]
2. development of new catalysts selective in total oxidation and resistant to deactivation by chlorine [89,90],
3. development of alternative technologies for removal of chlorinated hydrocarbons.

For the treatment of chlorinated hydrocarbons, the following technologies have been proposed:

- incineration, which is a high energy consuming process, producing very toxic atmospheric pollutants, such as phosgene and dioxins [91,92];
- catalytic gas phase and liquid phase hydrogenation which converts chlorinated hydrocarbons to other organic compounds, and therefore its application is limited to particular chlorine bearing compounds when the further use of the reaction products is envisaged [93–98].
- catalytic destruction of chlorine and fluorine containing compounds by water (catalysed hydrolysis) — an effective process, but studied only with a limited number of C_1 and C_2 halogenated hydrocarbons [99,100].

Other techniques such as plasma treatment [101], reduction in sodium naphtralenide [102] and destruction by supercritical water [103] have been reported and proved to be efficient in laboratory tests, but when scaled-up to the industrial level, difficulties in practical implementation or economics hindered the further development of these techniques [99].

For environmentally safe destruction of chloroorganic compounds, a new technology was developed at BIC by Buyanov et al. [104]. This technology consists of catalytic decomposition of chlorinated hydrocarbons to filamentous carbon, methane and HCl on supported Ni, Co and Fe catalysts.

The process was tested with various chlorinated hydrocarbons: CCl_4, $CHCl_3$, dichloroethane, chloropropanes, chlorobenzene, etc. and their mixtures. It was found that the balance of H to Cl in the treated substance has the substantial effect on the catalyst performance in the decomposition of chlorinated hydrocarbons. During the decomposition, chlorine atoms combine with hydrogen atoms to produce HCl, so it is necessary that the number of hydrogen atoms in the molecule should be equal to or exceed the number of chlorine atoms. Otherwise the chlorine formed deactivates the catalyst, e.g. in the case of chloroform $CHCl_3$ and CCl_4, the catalyst loses activity in 10 min. Stabilization of the catalyst activity in the decomposition of such compounds can be achieved by adding hydrogen to the initial reaction mixture, with the yield of carbon increasing from low values of less than $1\,g/g_{cat}$ without hydrogen to $7–24\,g/g_{cat}$. in the presence of hydrogen. The excess hydrogen may react with carbon to produce methane. In the case of compounds containing a sufficient number of hydrogen atoms to prevent chlorine formation, e.g. $C_2H_4Cl_2$, the process can be carried out efficiently both in the presence and in the absence of hydrogen, with carbon yields exceeding $100\,g/g_{cat}$.

Thus, the process can presented by the reaction:

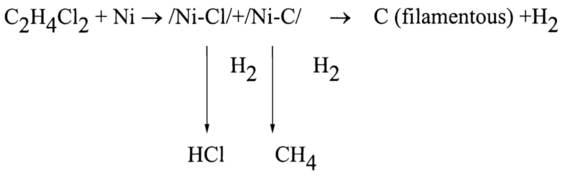
$$C_xH_yCl_z + (H_2) \xrightarrow{Ni} C + (CH_4) + HCl,$$

where the composition of the initial reaction mixture and reaction products depends on the balance of hydrogen and chlorine atoms in the molecule of the substance treated and the process conditions.

The study of the decomposition of $C_2H_4Cl_2$ in the mixture $C_2H_4Cl_2 : H_2 = 1 : 1.5$ and space velocity $30\,000\,h^{-1}$ showed that the main products of the reaction are carbon, HCl and unreacted H_2.. The yield of the carbon at 550°C attains 92–96% and the reaction rate appears stable for 6–7 h.

The reaction selectivity changes drastically when a large excess of hydrogen is added to dichloroethane. ($C_2H_4Cl_2 : H_2 = 1 : 10$), and the space velocity is reduced to $12\,000\,h^{-1}$. In this case the total $C_2H_4Cl_2$ conversion at 550°C is also very high — over 99%, but the main reaction products are methane and HCl. The carbon yield is less than 2%.

These observations allow the following representation of the reaction mechanism:



When the initial hydrocarbon is diluted by small amounts of Ar or H_2, the dichloroethane decomposes via a carbide cycle mechanism, forming carbon, HCl and hydrogen. In this case the hydrogen is consumed mainly for the hydrogenation of the surface nickel chloride.

With increasing hydrogen concentrations in the initial mixture, it is consumed also for hydrogenation of surface carbon; therefore, the yield of carbon decreases at the expense of methane formation.

This method was tested in application to real waste, containing over 20 organic compounds: $CHCl_3$, $C_2H_4Cl_2$, $C_2H_3Cl_3$, chlorinated propanes, butanes, pentanes, chlorobenzene, etc., and demonstrated a high efficiency of conversion of the compounds treated to carbon, methane and HCl.

Thus, this technique of destruction of chlorinated hydrocarbons can be considered promising, and should therefore be tested and evaluated for particular application in the removal of chloroorganic compounds from the off-gas of processes of groundwater air stripping in nuclear sites remediation.

7. Conclusions

In summary, various catalytic processes were studied for efficiency in particular applications of nuclear industry waste processing. Some of them, e.g. fluidized bed catalytic destruction of mixed organic wastes and NO_x abatement in gas streams using environmentally benign $DeNO_x$ catalysts, proved to be very effective and are ready for industrial implementation. The others are found promising and need to be further studied with particular waste streams of the Nuclear Industry. The most promising directions of research and the results obtained are given below.

1. The environmentally safe process for catalytic fluidized bed oxidation of mixed organic wastes has been developed and a prototype demonstration plant for processing of wastes containing isotopes of uranium has been built.
2. Destruction of organic compounds in catalytically active melts has been studied and is shown to be promising for mixed waste treatment.
3. Environmentally benign catalysts for SCR of NO_x in off gases of plasma processing of mixed waste have been developed and successfully tested.
4. A method for catalytic removal of H_2 from tanks with liquid radioactive wastes has been proposed

and suitable hydrophobic catalysts have been developed.

5. A new catalytic method for destruction of chlorinated hydrocarbons with formation of filamentous carbon, CH_4 and HCl has been developed.

On the whole, the above achievements show that catalysis can be used as a powerful tool to improve efficiency and environmental safety of nuclear waste storage, processing and disposal.

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