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Prevention and Remediation In Selected Industrial Sectors

BEST AVAILABLE ECOLOGICAL FRIENDLY TECHNOLOGIES FOR UTILIZATION OR DESTRUCTION OF POP's IN THE RUSSIAN FEDERATION

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Introduction

- Persistent organic pollutants (POPs) are related to highly toxical chemical substances which are negatively influence on people's health and environment.
- From 12's of POPs included in the Stockholm Convention by enterprises of the Russian Federation up to 1993 have been manufactured polychlorbiphenyls (PCB), hexachlorobenzene, toxaphene and DDT, after that all these enterprises were closed.
- The Russian Federation signed the Stockholm Convention on POPs in 22 May, 2002 (The Resolution of the Government of the Russian Federation №320 from 18 May, 2002) and now is carrying out the preparation of its ratification.

Activity on reduction and prohibition of POPs use within the performance of the Stockholm Convention at preparation of National Implementation Plan:

- Carrying out of national inventories on POPs and the PCB containing equipment;
- Gathering the information on POPs management and on technologies of their processing and destruction;
- Preparation of national strategy and plans of action on reduction and prohibition of POPs use;
- Definition of the key organizations, stakeholders and experts in the country for performance of this activity;
- Association and concentration of joint efforts of authorities, owners of the enterprises and the public for the decision of POPs problems

The revealed problems

- Absence of sufficient coordination not only at a federal but also at regional and local levels at carrying out of inventory of stocks and planning actions;
- Weak interest of owners of the enterprises in actual data about POPs presence;
- Insufficiency of technical capacities for a full and ecologically comprehensible method of POPs destruction, restoration of the polluted territories;
- Necessity of carrying out of an additional estimation of ecological conditions for area of the industry made POPs, warehouses of storage and other pollution sources;
- Requirement for carrying out of full complex POPs inventory and the conditions of their storage which are being restricted areas;
- Insufficient quantity of domestic technologies on POPs destruction passing by the state ecological expertise at federal and regional levels;
- Insufficient quantity of the corresponding accredited laboratories, the out-of-date equipment of monitoring systems for selection and the analysis of tests;
- Frame character of many Russian laws demanding for the realization development and introduction the big number of subordinate acts.

Methods of POPs neutralization

The problem of destruction/neutralization of persistent organic pollutants (POPs) such as polychlorinated biphenyls, hexachlorobenzene, pesticides (DDT, toxaphene, polychlorpinene, polychlorcaphene) in the Russian Federation has not been solved yet.

Methods of POPs neutralization existing in the Russian Federation by analogy to global practice can be divided into **three variants**:

- **Ground disposal** of PCB containing waste with observance of effective standards, safety rules and actions on preservation of the environment;
- **Chemical treatment** of POPs with reception of nontoxic substances;
- **Destruction** of POPs.

Ground disposal

- From the technological point of view it is a simple operation.
- From ecological - the ground disposal fulfilled according to normative requirements **does not liquidate danger** which can arise again.
- Concerns to the way of POPs neutralization postponed in time by any accessible method.
- Now on the territory of the Russian Federation there are 4 operating waste's polygons used in Tomsky, Leningradsky, Kaluzhsky and Omsky regions for **ground disposal**.

Polygons for ground disposal of POPs

- **The State enterprise "Polygon" (Tomsky region)**

  Wastes of I-III classes of danger to environment including Hg containing waste and the PCB containing waste; HCCB and other POPs.

  The license validity till 2010.

- **The State polygon «Krasniy Bor» (Leningradsky region)**

  Wastes of I-IY classes of danger to environment including Hg-containing waste; the PCB containing waste; not identified pesticides with expired validity. The license validity till 2009.

  Now the polygon is on reconstruction.

- **The polygon ASEKO (Kaluzhsky region, Obninsk)**

  Wastes of I-III classes of danger to environment, including waste of pesticides, dry waste of galvanic, delayed chemicals are placed.

  The license validity till 2009.

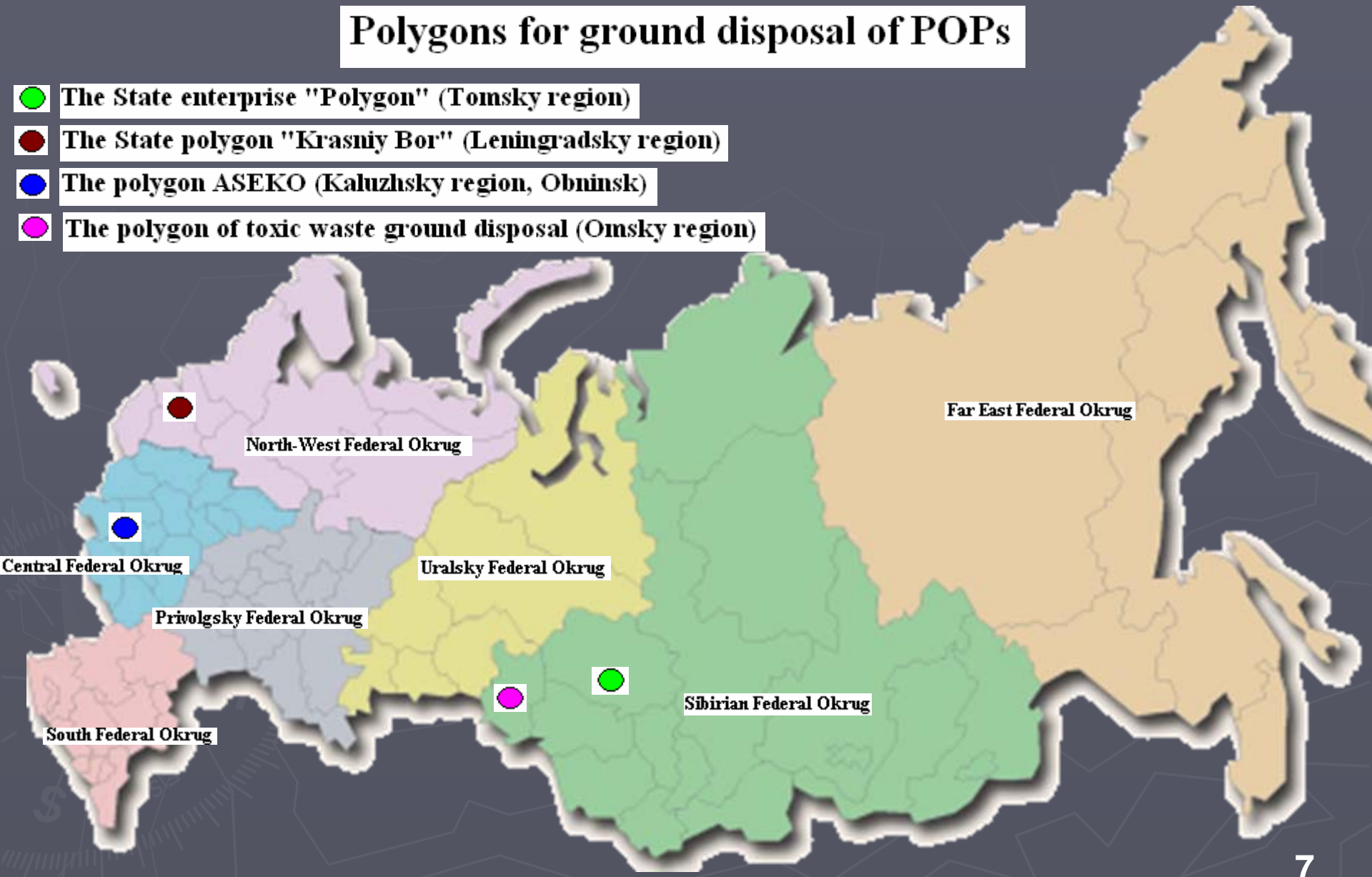
- **The polygon of toxic waste ground disposal (Omsky region)**

  Wastes of I-IY classes of danger to environment including Hg-containing wastes; wastes of the pesticides forbidden to application and with expired validity.

  The license validity till 2009.

The given quantity of polygons obviously is not enough. Existing conditions of ground disposal often do not correspond the requirements, there is a set of cases of outflow or passages in an environment.

Polygons for ground disposal of POPs



Russian accredited laborites for POPs analyses

There are 4 accredited Russian laboratories using international methodology and standards for dioxins, furans and other POPs sample analyses:

- **The Bashkir's Research Ecological Center of Bashkortostan Ministry for Natural Resources, Ufa, Republic of Bashkortostan;**
- **Institute of Ecology and Evolution Problems named after N.A. Severtsov, Russian Academy of Sciences, Moscow;**
- **NPO "Typhoon" of Roshydromet, Obninsk, Kaluzhsky region;**
- **FSE "Russian Science and Research Center for Emergencies" of the Federal Medical and Biology Agency, Moscow.**

Russian accredited laborites for POPs analyses

MOSCOW

Institute of Ecology and Evolution Problems named after N.A. Severtsov, Russian Academy of Sciences

FSE "Russian Science and Research Center for Emergencies" of the Federal Medical and Biology Agency

OBNINSK, Kaluzhsky region

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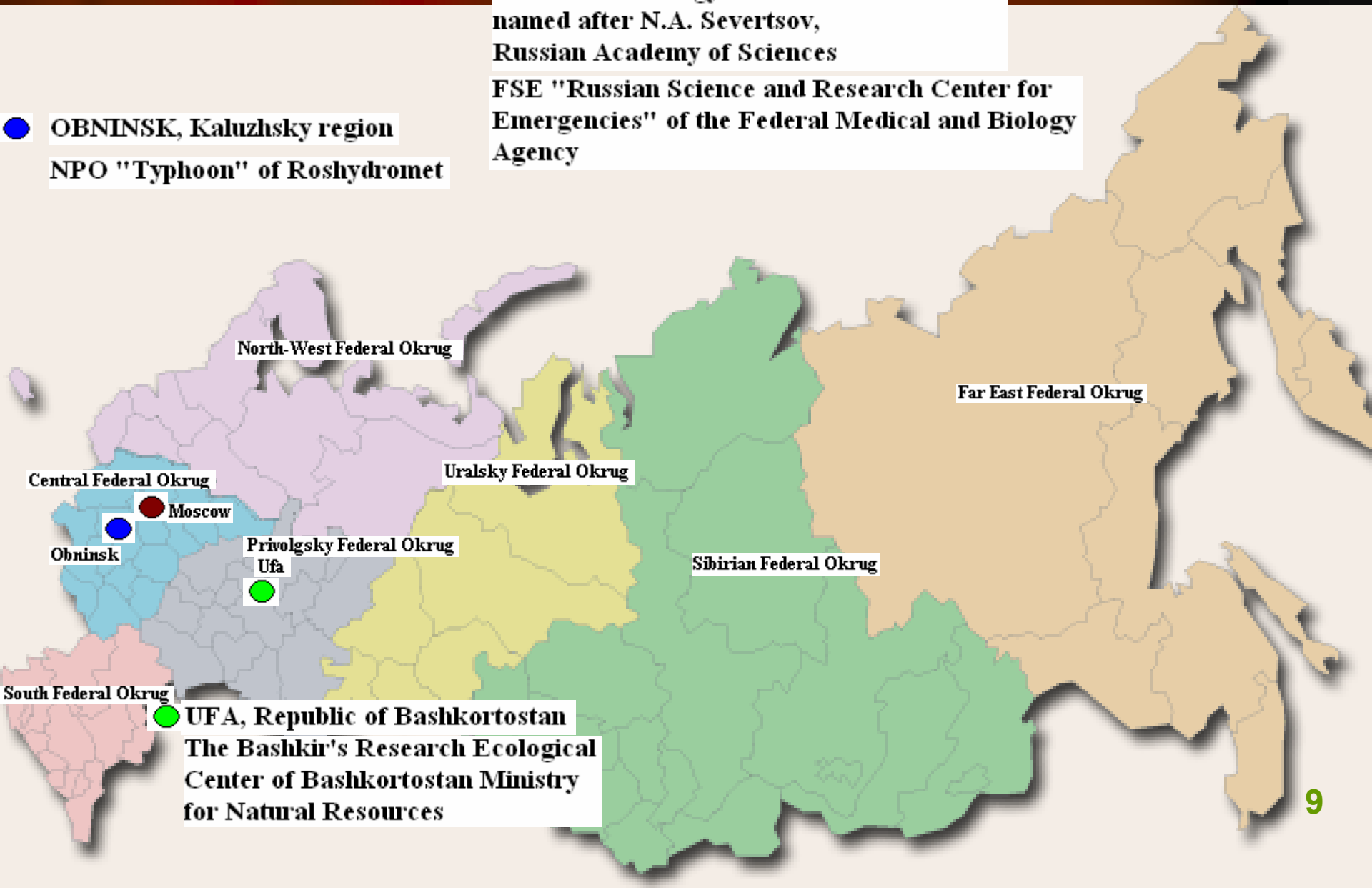


UFA, Republic of Bashkortostan

The Bashkir's Research Ecological Center of Bashkortostan Ministry for Natural Resources

Technologies of POPs Treatment and Destruction

- **In the developed countries** the liquid POPs waste containing **less than 1 % of PCB weight** therefore **is guaranteed obtaining of harmless products** in which PCB contents does not exceed **50 ppm**.

  Cost of chemical treatment of PCB-containing waste ranges from 2000 till 4000 US dollars per 1 ton of PCB.
- The existing **Russian technology** of chemical treatment of liquid waste is considered on PCB contents **up to 90 %.**

  In the advanced waste PCB contents exceeds over 50 ppm, that by the European specifications **carries them to dangerous**, and **demand destruction or a ground disposal** on special polygon.

  Cost of such chemical treatment of 1 ton of PCB is about 3000 US dollars.

- The foreign experience of POPs destruction show that **the main technological method of utilization is a highly temperature oxidation** with application of reactors having different constructions. **The main technologies** of highly temperature oxidation are:
- installation including rotational furnace;
- installation including stationary furnace;
- installation with the liquid waste injection;
- installation with plasma chemical technology

The Russian methods of POPs destruction

- There are **some methods of POPs and other chlorine-containing wastes destruction** in Russia. Now it is accepted to combine destruction of **liquid unsuitable pesticides** and polychlorinated biphenyls as technological parameters and hardware registration completely coincide.
- Installations for destruction of **solid** and **paste** like POPs are similar with installation for destruction of liquid POPs with some modernization by adding of the special mixing equipment.
- **The most perspective methods of high temperature oxidation:**
  - High-temperature furnaces with a cyclonic reactor;
  - Combustion chambers of high-temperature rocket engines;
  - Installations on the basis of liquid rocket engines;
  - Installations on the basis of plasma chemical technologies;
  - Destruction in a stream of the heated gases;
  - Explosion of the explosive containing chemically neutralized PCB;
  - Fuel combustion at high-temperatures and contact heating;
  - Blast-furnaces;
  - Cement kilns.

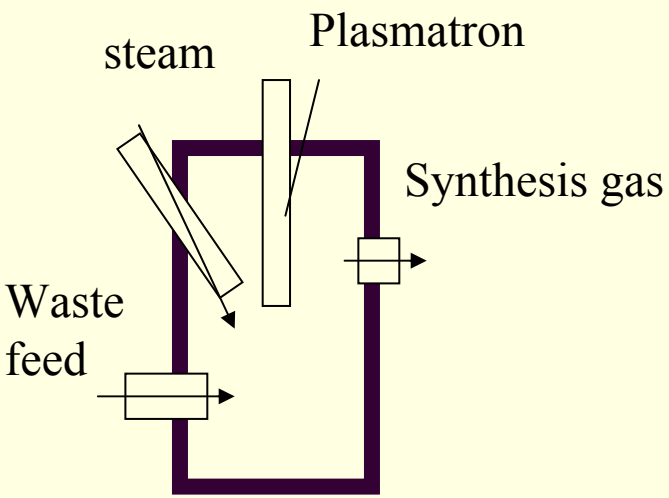
Russian technologies of high-temperature oxidation (for POPs destruction)

On the basis of the considered **technical, ecological and economic requirements to technologies** of POPs destruction were developed **four** Russian technologies of high-temperature oxidation with using:

- thermodestruction in cyclonic reactor (Author – JSC«Techenergochimprom», Moscow and Orekhovo-Zuyevo, the Moscow region);
- The rocket engine (Author – ZNIIMASH Korolev; the Moscow region, Open Society "Severstyle" Cherepovets, the Vologda region);
- The liquid rocket engine (Author– INCC of the Russian Academy of Science, Moscow, Federal State Enterprise «Voenmech», St.-Petersburg);
- The plasmatron and a chemical reactor:
  - the traditional approach (Author -RNC «Prikladnaya Chemistry», St.-Petersburg);
  - the new construction (Author – International Centre of Thermal Physics and Power Engineering (ICTP&PE), Novosibirsk, Russia).

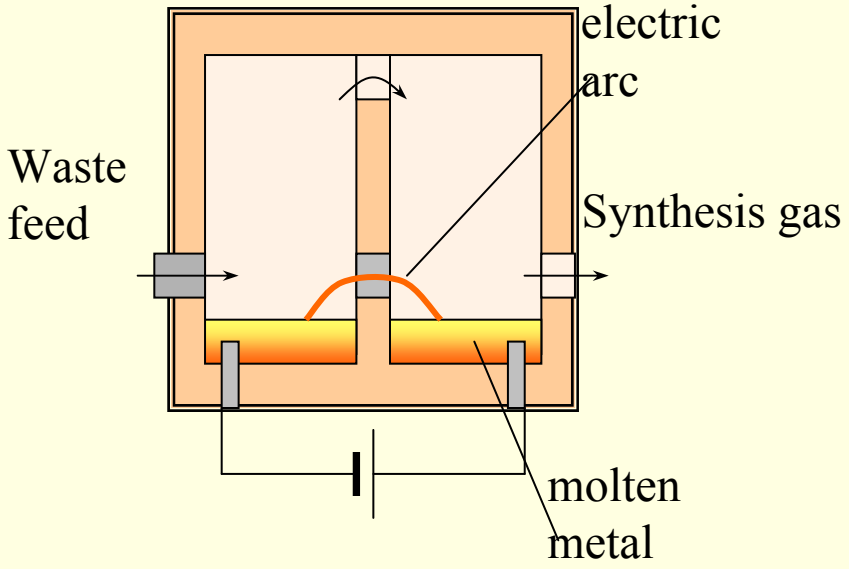
Plasma chemical reactor for destruction of POPs containing wastes developed by ICTP&PE(Novosibirsk, Russia)

Traditional scheme



$$C_nH_mCl_k + nH_2O \rightarrow CO + H_2 + HCl$$

New construction



Lacks

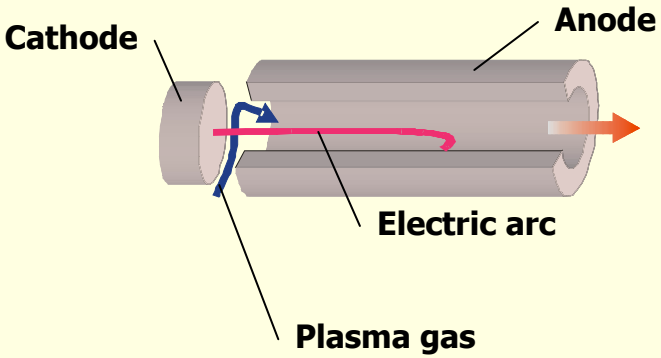
- A low resource of plasmatron (erosion of electrodes)
- Plasma gas - Ar, air
- Insufficient depth of processing

Advantages

+ the Long resource of continuous work
+ the Opportunity of use steam as plasma gas
+ the High degree of processing

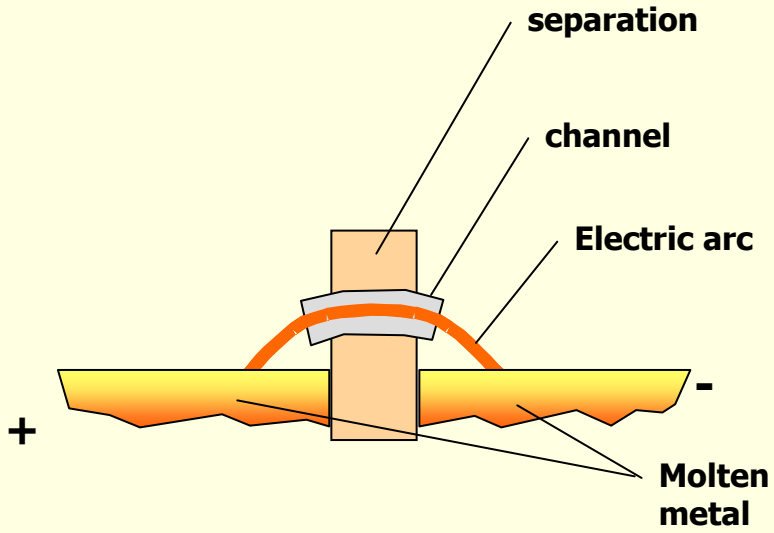
Plasmatron with liquid metallic electrodes

Typical plasmatron



Erosion of electrodes

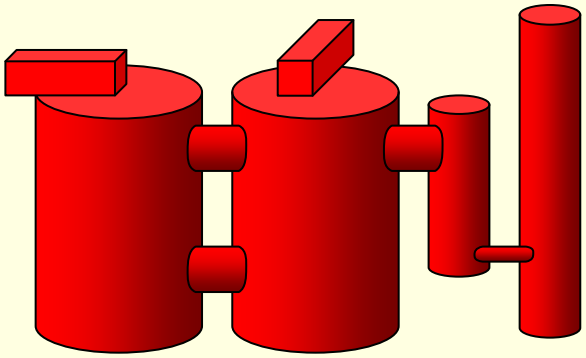
Plasmatron with liquid metal electrodes

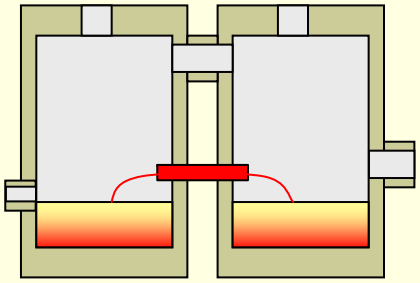


No erosion of electrodes

- \+ no limited resource of electrodes
- \+ large capacity
- \+ high affectivity
- \+ plasma gas – steam

Plasma Chemical Reactor (PCR-500)





Plasma torch power	500 kW
Plasma gas	Steam, air or nitrogen
Gas flow rate	50-150 kg/h
Waste capacity	Up to 200 kg/h

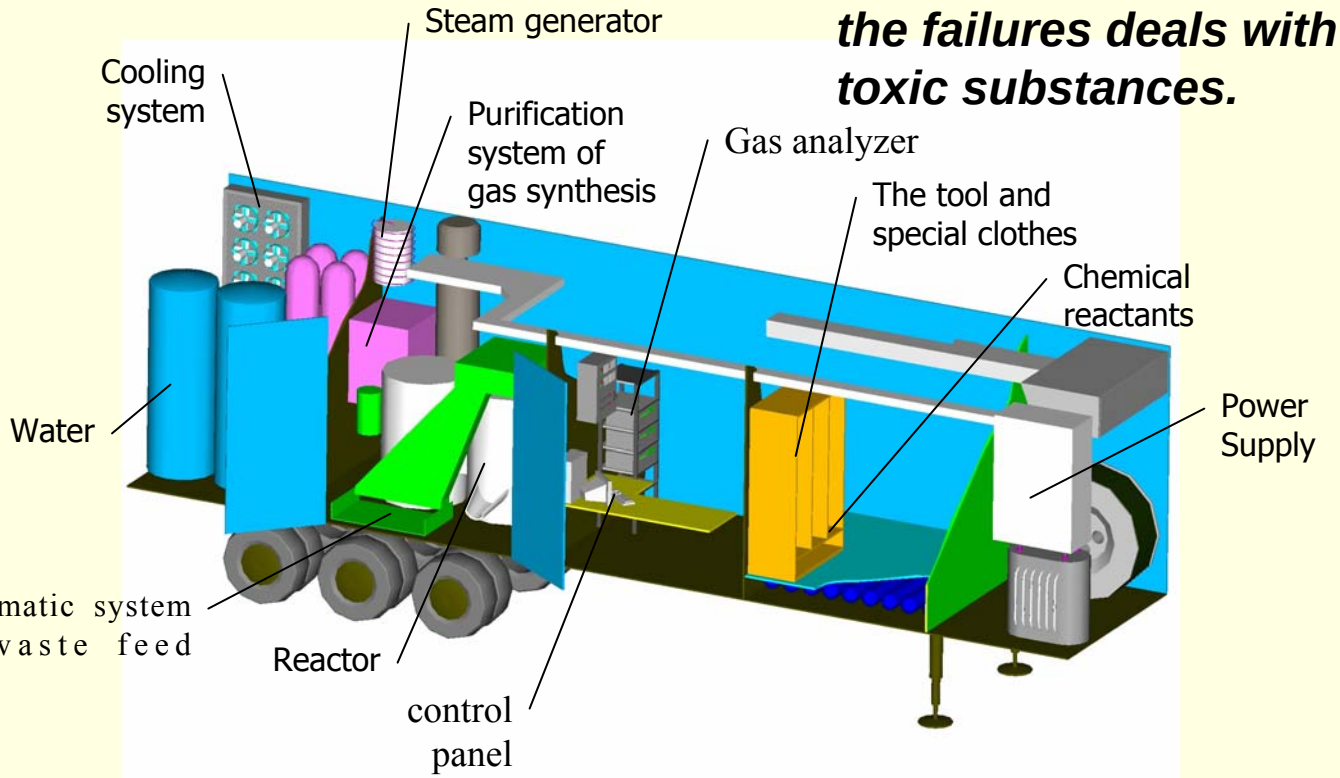
Analysis of dioxin's concentration in gasification products of chlorine containing hydrocarbons

Reactants	*Modeling mixer* (isopropyl alcohol + benzene + CCl_4)	*Modeling mixer* (isopropyl alcohol + benzene + CCl_4)	TCB (trichlorbiphenyl)
Chlorine concentration	10%	20%	40%
Plasma gas	Air, modeling of garbage burner	steam	steam
Reactor temperature, °C	1100	1300	1300
Concentration of dioxins in reaction products, TEQ, ng/Nm3	20	0,02	0,05

- According to the European specification the maximum of dioxin's content in industrial emissions - TEQ is not more 0,1 ng/Nm^3

Mobil installation of plasma destruction of toxic wastes

Destruction of super toxicants on places of storage, liquidation of the failures deals with flood of toxic substances.



Capacity	up to 100 kg/h
Supplied electric power	250 kW

Comparison of POPs destruction methods on technical and economic parameters

- On the basic economic parameters - advantage of the high-temperature oxidation technology with use of a cyclonic reactor has costs of creation of installation and cost of processing of 1 ton of POPs.

The basic economic parameters of the Russian technologies of POPs destruction

(In thousand US dollars on the prices of January, 2007)

Methods of POPs destruction	Cost of R&D	Cost of installation development			Expenses on destruction of 1 t of POPs	
		Cost of design	Capital cost	Summary cost	Prime cost	Price
Thermodestruction in cyclonic reactor	100	200	1800	2100	1000	1200
The rocket engine	200	200	2200	2600	1200	1400
The plasmatron and a chemical reactor	**Traditional scheme/ New construction**					
	200	200	3500	3900	1700	2000/ 500
The liquid rocket engine	200	200	2000	2400	1200	1400

Estimation and Comparison of PCB cleaning methods of the polluted transformers and containers

Technologies of neutralization applied now in a world practice are realized by washing of transformers and containers and are divided on **two basic groups**.

- The **first** group (most numerous) concern technologies of washing from PCB with the subsequent liquidation of transformers and containers.
- The **second** group (small) include washing technologies of an internal part of transformers from PCB and the subsequent filling them with an alternative liquid (retro filling).
- **After drainage of a PCB-containing liquid** transformers, condensers and containers are considered as the PCB polluted wastes which are necessary **for utilizing in ecologically comprehensible way.**

Foreign technologies of PCB neutralization of the polluted transformers are divided on two groups

- **The first group** unites washing from PCB technologies with the subsequent liquidation of transformers and containers. The principle of work consists in **preliminary washing the transformer « in gathering »,** then to its disassembly and additional washing metal details up to PCB contents on their surface less than 50 ppm (mg/kg) which corresponds Instructions of EU concern **to harmless waste** and can be utilized by any comprehensible way.

  Remained from the transformer disassembly the wooden and cardboard wastes containing more 50 ppm (mg/kg) of PCB are burnt.

- **The second group** unites washing from PCB technologies of an internal part of transformers with the subsequent filling with an alternative liquid (retro filling).

  Such technologies are small in number.

  The **economically effective** technologies are concerning **the first** group.

Russian technologies of transformers and containers washing from PCB

A. Three existing Russian technologies of transformers and containers washing from PCB has shown that all of them concern to technology of 1 group:

- **washing from PCB by vapors of chloride methylene** which is recommended by JSC “PetrochimTechnologiya” together with RNC “Prikladnaya Chimiya” after check in skilled scale;
- **washing from PCB by toluene** is presented by enterprise "GITOS" after experimental test;
- **washing from PCB by water washing solutions** is recommended by Novo Lipetsk’s metallurgical combine after experimental test.

These Russian washing technologies are stipulated **cleaning** of PCB transformers **only “in gathering”** with their subsequent disassembly and utilizing of metal details.

B.

- The preliminary **technical and ecological estimation** has shown, that at realization **of technology washing from PCB by a water washing solution** is reached a residual PCB content on metal details nearby **5000 ppm** that relates them to **very dangerous wastes** and demands additional measures and means on their destruction or ground disposal.
- Comparison **of technological schemes of washing from PCB** has shown that **the technology with use of toluene is more complex** in comparison with **technology with use of methylene chloride**.
- Comparison **of ecological** characteristics **of the two first Russian technologies** of washing from PCB transformers and containers has shown, that **by both technologies is reached completeness of clearing of the metal details, corresponding requirements of EU (less than 50 ppm).** However, unlike technology with **methylene chloride in which there are no sewage** and firm waste, in technology with **toluene is formed polluted PCB sewage** and the solid waste demanding additional clearing.

C.

- **Installation of clearing from PCB with use of methylene chloride** roughly **costs - 750 000 US dollars**,

  Cost of carrying out of one operation **(treating of 1 transformer)** on technology with use **of methylene chloride - 1200 US dollars.**
- **Cost of installation with use of toluene roughly- 870 000 US dollars**.
- Cost of carrying out of one operation **(treating of 1 transformer)** by technology with use **of toluene - 2000 US dollars**.

- Estimation of cost proceed from 100 operations per year that corresponds to treating of 100 transformers per year on one installation.

- According to **technical, ecological and economic characteristics** of washing methods from PCB transformers and containers **in Russia it is recommended the technology with use of chloride methylene vapors** as solvent.
- Creation and using of **mobile variant** of such installation with above mentioned technology is also capable in certain circumstances (transport infrastructure, features of territories, etc.).

Comparison of destruction methods of PCB containing condensers

- **International industrial practice of destruction / neutralization processes of PCB containing condensers are carried out according with two dimensions:**

1. **Destruction** of condensers which have been preliminary crushed by applying of **high-temperature burning**. Cost of such a process is about 1600 US dollars per 1 ton of condensers.
2. **Neutralization** of condensers with the subsequent recycling of metals includes washing condensers, their disassembly, the second washing of cases and cores. Cost of processing of 1 ton of condensers is about 2200 US dollars.

Russian Technologies of condenser's neutralization

A.

There are divided into **two** dimensions

- **First** dimension using the following **methods of burning**:

- Explosion of the explosive containing chemically neutralized PCB in particles of crushed condensers;

- Fuel in high-temperature powder like mixes of filtration burning (PMFB);

- Bubble melting furnace with systems of fuel depletion and neutralization of tail gases.

According with ecological parameters: 2 first's methods are not recommended because there are no guarantees of absence as PCB or dioxins in emissions. Completion is necessary.

- **Second** dimension mostly use **the method of** condensers **kilning**.

These neutralization technology based on condenser kilning with subsequent metal recycling was approbated on Novolipetsky enterprise and not recommended yet for using in Russia because it is unknown the degree of PCB convergence and dioxins contain in tail gases. Also completion is necessary.

B.

- According to **technical, ecological and economic** parameters **bubble melting furnace technology with systems of fuel depletion and neutralizations of tail gases** is recommended for using in the Russian Federation.
- Technological conditions allow to consider this technology as corresponding the European requirements (a degree of PCB neutralization- not less than 99,9999 %, the dioxins contents in tail gases - less than 0,1 ng/m^3).

  Cost of such installation by productivity 4000 t of condensers per year - 2,6 million US dollars, and cost of processing of one ton of condensers - about 1500 US dollars.

- Besides the **high-temperature cyclonic reactor technology of solid and paste like POPs destruction** is also recommended by Company «Synthesis» (Moscow) for using in Russia.

C.

- **Further more these installations** can be used **for destruction of other dangerous waste**, including unsuitable sulphur-, nitrogen-and phosphorous containing pesticides.
- **Capacity of installation:**

  - destruction of solid and paste like POPs - from 300 kg till 500 kg per hour;

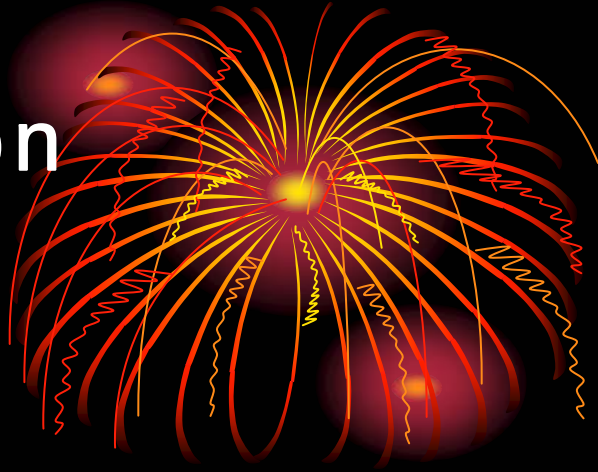
  - destruction of liquid POPs - 100-200 kg per hour.
- **Cost** of the process equipment and assemblage of each installation is roughly 1,8 million US dollar.

- While using the high-temperature technology of POPs burning in **a cyclonic reactor** are formed solid **wastes** and the gas **emissions** consisting of carbon oxide and dioxide, nitrogen, traces of hydrogen chloride, organic carbon and there parameters **are correspond to the requirements of the** EU Directive 00/76/EU.

Conclusions

- The period from the beginning of the development of new technology and installation for POPs destruction proceeds for a long time.
- The development of new technology and installation for POPs destruction demand sufficient financial government and private investment support.
- According to Federal Act of the Russian Parliament from 23.11.1995 №173-FA “About the Environmental Expertise” every new technology influence on environmental require conclusion of the Federal (regional) Environmental Expertise.
- The number of the existing and operating technologies on POPs destruction in the Russian Federation with the positive conclusions of the Federal (regional) Environmental Expertise is imperceptible. That demands increase of the Government attention to the given problem including the development of the National Implementation Plan.

Thank you for your attention



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