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

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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- Insufficient quantity of the corresponding accredited laboratories, the out-of-date equipment of monitoring systems for selection and the analysis of tests;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

- The State enterprise "Polygon" (Tomsk region)
- The State polygon "Krasniy Bor" (Leningradsky region)
- The polygon ASEKO (Kaluzhsky region, Obninsk)
- The polygon of toxic waste ground disposal (Omsky region)
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
NPO "Typhoon" of Roshydromet

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)

**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

C<sub>n</sub>H<sub>m</sub>Cl<sub>k</sub> + nH<sub>2</sub>O → CO + H<sub>2</sub> + HCl
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)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma torch power</td>
<td>500 kW</td>
</tr>
<tr>
<td>Plasma gas</td>
<td>Steam, air or nitrogen</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>50-150 kg/h</td>
</tr>
<tr>
<td>Waste capacity</td>
<td>Up to 200 kg/h</td>
</tr>
</tbody>
</table>
Analysis of dioxin’s concentration in gasification products of chlorine containing hydrocarbons

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Modeling mixer (isopropyl alcohol + benzene + CCl₄)</th>
<th>Modeling mixer (isopropyl alcohol + benzene + CCl₄)</th>
<th>TCB (trichlorbiphenyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine concentration</td>
<td>10%</td>
<td>20%</td>
<td>40%</td>
</tr>
<tr>
<td>Plasma gas</td>
<td>Air, modeling of garbage burner</td>
<td>steam</td>
<td>steam</td>
</tr>
<tr>
<td>Reactor temperature, °C</td>
<td>1100</td>
<td>1300</td>
<td>1300</td>
</tr>
<tr>
<td>Concentration of dioxins in reaction products, TEQ, ng/Nm³</td>
<td>20</td>
<td>0,02</td>
<td>0,05</td>
</tr>
</tbody>
</table>

• According to the European specification the maximum of dioxin’s content in industrial emissions - TEQ is not more 0,1 ng/Nm³
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)

<table>
<thead>
<tr>
<th>Methods of POPs destruction</th>
<th>Cost of R&amp;D</th>
<th>Cost of installation development</th>
<th>Expenses on destruction of 1 t of POPs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cost of design</td>
<td>Capital cost</td>
</tr>
<tr>
<td>Thermodestruction in cyclonic reactor</td>
<td>100</td>
<td>200</td>
<td>1800</td>
</tr>
<tr>
<td>The rocket engine</td>
<td>200</td>
<td>200</td>
<td>2200</td>
</tr>
<tr>
<td>The plasmatron and a chemical reactor</td>
<td>200</td>
<td>200</td>
<td>3500</td>
</tr>
<tr>
<td>Traditional scheme/ New construction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The liquid rocket engine</td>
<td>200</td>
<td>200</td>
<td>2000</td>
</tr>
</tbody>
</table>
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/m³).

  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.
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.
- 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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