Overview on the waste material from the former lindane plant in Skopje

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Introduction

The lindane complex in AD OHIS - Skopje had the plants producing HCH, lindane, trichlorobenzene (TCB) and hydrochloric acid. These plants formed a united technological circle supporting each other. In the HCH plant, the technical hexachlorocyclohexane with gamma isomer represents 12-14% was produced through the syntheses of chlorine and benzene. This technical HCH provided the raw material for obtaining pure gamma-isomer 99,9%, i. e. lindane, while the non-active isomers such as alpha, beta and delta which were extracted in the lindane plant provided the raw materials for obtaining trichlorobenzene and hydrochloric acid in the TCB Plant.

The extraction process of the gamma isomer from HCH was performed using methanol as a solvent and had a flow pathway in the process, but didn't take part in the process itself. While trichlorobenzene and hydrochloric acid were produced from the non-active isomers using thermal dissolution in the presence of active coal as a catalyst.

The lindane complex was gradually put into operation by a license issued by the German firm C.H. Boehringer Sohn from Ingelheim am Rhein since 1964. It was functioning until 1977, when it was abandoned and stopped for ecological reasons and the change of the market conditions and needs.

Factors responsible for abandoning lindane production in OHIS

Abandoning production of lindane in OHIS was attributed to some factors, the most important of which are as follows:

1. The absence of appropriate technology for utilisation of the non-active isomers in more valuable products, during the production of lindane, with 86% of the HCH produced as non-active isomers. These isomers were treated as wastes, although in some firms they considered as valuable materials for obtaining certain kinds of insecticides and fungicides.
2. The small production capacity of the plant couldn't match or stand the market competition with other plants, which had ten fold production capacities compared to our plant.
3. Marketing problems for lindane and trichlorobenzene.

   In the former Yugoslavia and worldwide as well, there was no market to trichlorobenzene, so the plant was not functioning for a long period of time. Moreover, the annual needs of lindane on the Yugoslavian market were also very little, about 80-120 tonnes, and it was less than 50% of the production capacity of the plant. The possibilities for worldwide marketing were small because of the substitution of the lindane with other preparations that were more effective, less toxic and cheaper.
4. The decreased utilisation of lindane was a consequence of the prohibition and use restriction.
5. The large amounts of the non-active isomers produced, the ecological impact of lindane beside financial, transport and storage problems made lindane production even more expensive.

Almost every limited producer of lindane in Europe faced similar problems and almost had the same destiny where they were forced to shut down the HCH and lindane production plants. These factors and the large stock of the product in the twelve years production strongly encouraged OHIS to abandon the production of lindane during 1977. After stopping the production, there were about 3,000 tonnes delta paste (delta isomer of the hexachlorocyclohexane) and about 30,000-35,000 tonnes mixture of alpha + beta isomer of HCH properly stored in "Biljana"- OHIS.

Physical and chemical characteristics of the waste material

The mixture alpha + beta-isomers of HCH

Chemical formula	$C_6H_6Cl_6$
Appearance	White powder
Smell	Unpleasant, like naphthalene
Particle size	40-80 microns
Molecular weight	290,9
Thickness	d=1.95
Melting point	183 ^{O}C
Solubility	Insoluble in water
Soluble in acetone, methanol and other organic solvents	

Average composition of the mixture

Alpha-isomer	84.75%
Gamma + Epsillon	0.55%
Beta-isomer	12.27%
Water contents	0.5%
Methanol	0.5%

Elemental composition of C_6H_6Cl

C	24.7%
H	2.06 %
Cl	73.20%
Heat combustion	2,700 kcal / kg chlorine
Deposition weight of alpha + beta waste (dry weight)	
a) By shaking	0. 608 g / ml
b) Non-shaking method	0.888 888 g / ml

B) Characteristics of delta paste

Appearance	Dark brown substance
Smell	Unpleasant (similar to HCH)
Solubility	Insoluble in water
	Soluble in acetone, methanol and other organic solvents.
Specific weight	0.950 at 20 °C
At a temperature of 50-60°C it changes to viscous liquid	

Composition of HCH-isomers in delta paste

Alpha	22-26%
Beta	5- 7%
Gamma	16-19%
Delta	38-50%

The paste contains also certain percentages of chlorinated benzenes and oily substances of unknown chemical composition.

Toxicity on rats

The toxicity of some of HCH isomers on the rats measured as LD_{50} is as follows:

Alpha LD_{50}	500 mg / kg
Beta LD_{50}	6,000 mg / kg
Gamma LD_{50}	125 mg / kg
Delta LD_{50}	1,000 mg / kg
Epsillon LD_{50}	1,000 mg / kg

HCH is not flammable or explosible

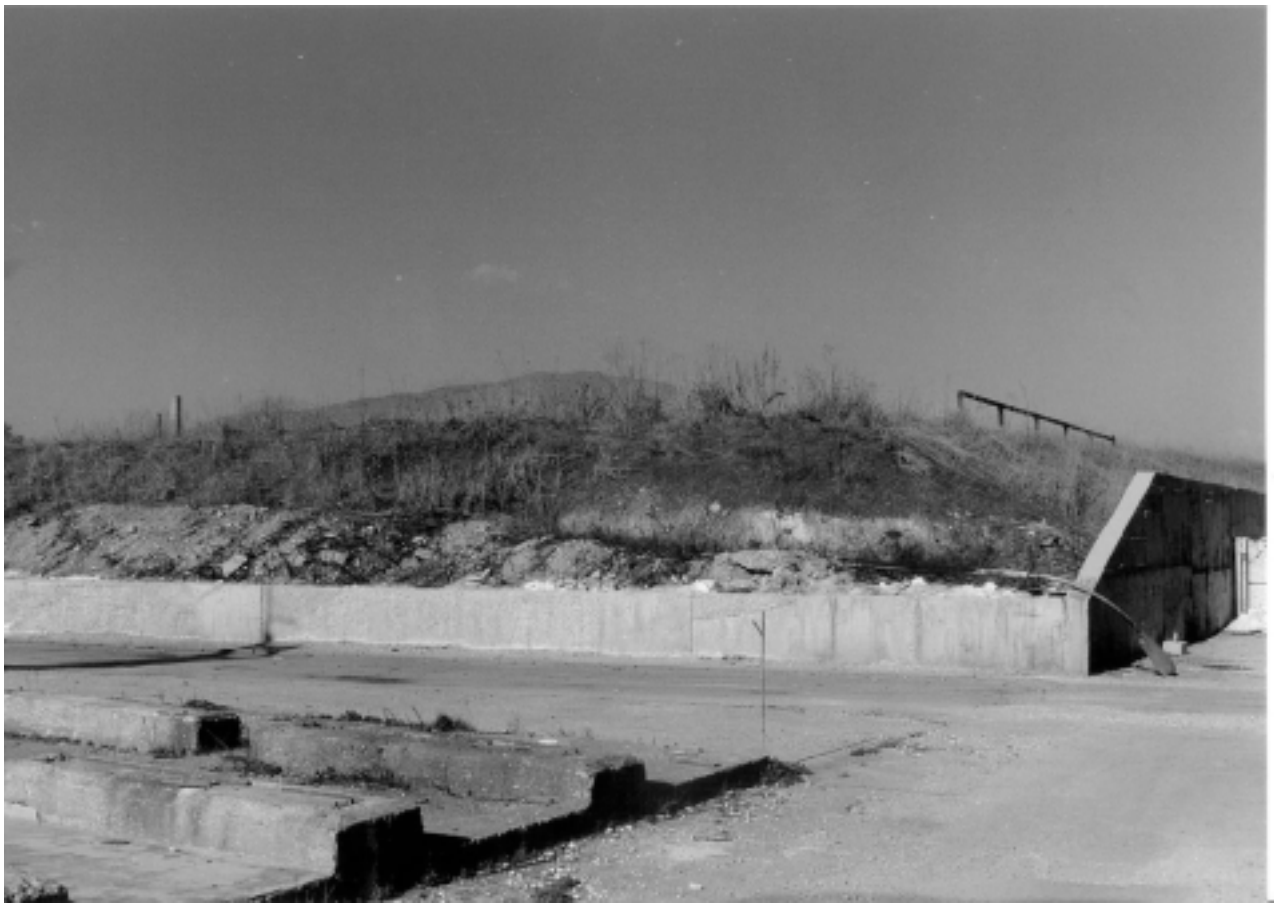

Figure 1. Alpha and Beta storage near view

Figure 2. Alpha and Beta storage overview

Figure 3. Delta-isomer storage near view

Management of the waste material

Some specialised firms for waste management have been consulted concerning the incineration of the non-active HCH-isomers and their transformation into more valuable products acceptable by the market. These firms included:

- Rimnicu Vilcea, Romania
- Krebs, Switzerland
- Efluterm, France
- Nittetu, Japan
- Chloe Chimie, France

The offers submitted by "Nittetu" and "Chloe Chimie" were very similar and had the most appropriate and acceptable solutions. They offered the incineration as a solution, from which hydrochloric acid will be obtained, and steam of 15 Atm that can be used as energy. Therefore, the lindane wastes still represent a serious problem that has to be solved in the near future.

Our ideas about future possible solutions

Although the problem is huge, we see possible solutions only in co-operation with other problem owners or by means of international help. One of the options of co-operation with other problem owners, we have described below:

1. OHIS has neither technology/equipment nor finances to overcome this problem alone.
2. OHIS suggests all parties participating the Forum, with a similar problem as ours, to organise a mutual action for its solution.
3. Activities to be performed:
   - Organising a common team of specialists from the interested parties, that will work out a common project for HCH waste treatment at the locations of the parties.
   - The selected technical solution (bio or thermal catalytic destruction) should consist of mobile equipment, which after finishing the work at one location of each party, will be transferred to another location.
   - Financing of the specialists' team, working personnel of the facilities and equipment supply will be borne by all parties wishing to do that (to sign the mutual contract). The amount of participation will be according to the planned waste quantity of each partner.
   - The project includes planned price of the processed waste depending on the type/m3. The working costs for actually processed waste will be compensated from the amount of participation into the project
   - Schedule/dynamics of work and other rights and obligations to be agreed by contract between the parties
   - Upon termination of the work on the locations of the parties, the team could also continue working with the equipment on locations of other companies as well, which were not part of the founders of this project.

We consider that our option is optimal for more parties participating the Forum and the cheapest solution of our problems.