Name of Process: Catalytic Hydro-Dechlorination (CHD) **Applicable POPs wastes:** PCBs, Dioxins (PCDDs/PCDFs)	**Status:** Japan Environmental Safety Corporation (JESCO), which is wholly owned by the government, has established five regional facilities for the treatment of PCB's and operates them. The Osaka PCB waste treatment facility is a one of them that is under operation that uses the Catalytic hydro-dechlorination (CHD). A permit for the treatment of PCBs was given in August 2006. Since October 2006, commercial activities are ongoing and more than 200 tonnes of PCBs have been treated till March 2008. 52 successful trial runs have been carried out before the commercial production has been started.

Technology description:
CHD involves the treatment of wastes with hydrogen gas and palladium on carbon (Pd/C) catalyst dispersed in the paraffin oil. Hydrogen reacts with chlorine in halogenated waste to produce hydrogen chloride (HCl) and non-halogenated waste. In the case of PCBs, biphenyl is the main product. The process operates at atmospheric pressure and temperatures between 180 °C and 260 °C (Ohno and Hirata, 1997, Noma et al, 2002, Noma, Ohno and Sakai, 2003)

1. Chemical reaction of CHD:

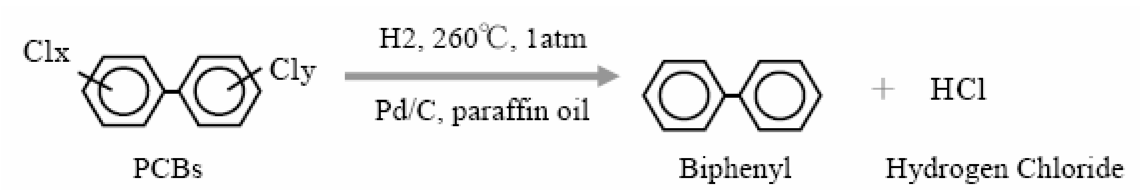

Figure 1: Chemical reaction of CHD

2. Flow diagram of reaction:

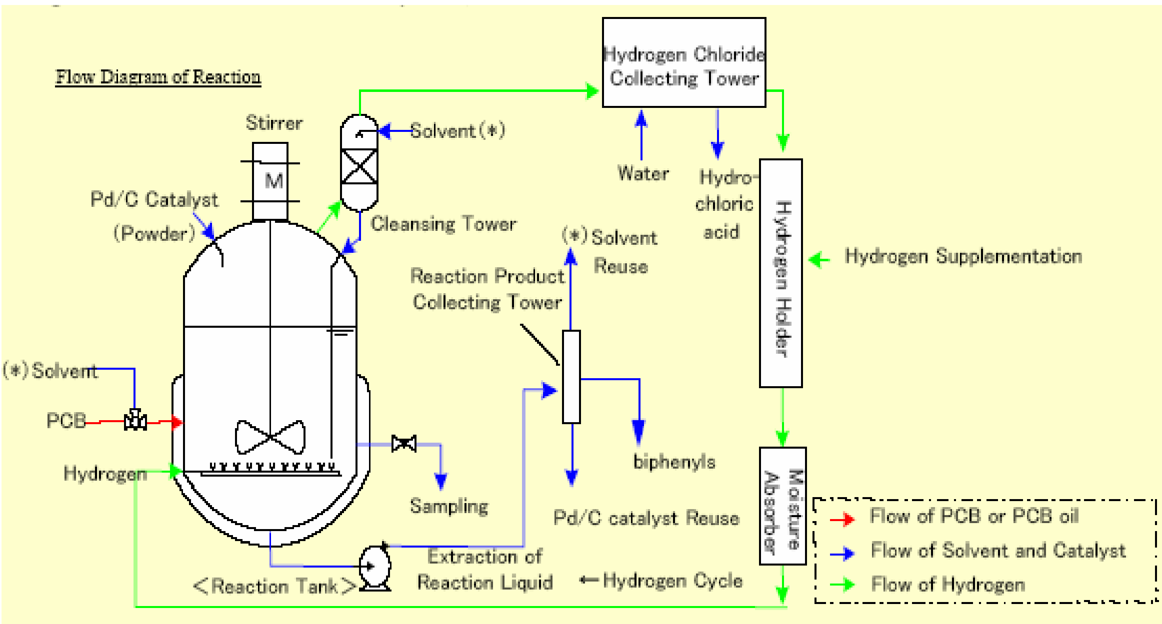

Figure 2: Flow diagram of reaction

The Osaka facility has two reaction systems of the same type. The PCB decomposition is a batch reaction. Maximum 250kg of PCB can be treated in one batch reaction. One batch reaction needs 6 hours, 4 batches can be run in a day for one system. This gives a maximum daily capacity to 2 tonnes of PCB in the facility. PCB decomposition takes place as follows. 2250kg of paraffin oil, which is the reaction solvents, and 34 kg of catalyst (Pd/C) is charged into the reactor in advance. Circulation of hydrogen gas through the reaction liquid is started under a normal pressure, and the reaction temperature is controlled at 260 □. PCB oil is prepared from the used transformers and capacitors. Extracted PCB oil from transformers is separated into PCB and TCB (Trichlorobenzene) by distillation (Tr-P). PCB contained in capacitors is collected at oil scrubbers by heating in vacuum (VTR-P). The prescribed volume of PCBs is injected into the reactor in one hour. Decomposition starts at the moment that PCB is injected. After finishing the PCB injection, the reaction goes on for 2.5 hours, the contents in the reactor is sampled for analyzing PCB concentration. PCBs, biphenyl and HCl leave from the outlet of the reactor with a hydrogen gas flow in the reaction period. Showering of the solvents at the outlet of the reactor stops PCBs and biphenyl leave from the reactor. HCl is absorbed by water at the water showering tower next to the solvent showering tower and collected as a hydro-chloric acid. Unreacted Hydrogen gas is cyclically reused.

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To hold the hydrogen gas pressure in the system, fresh hydrogen gas produced by a water electrolysis system is supplied. After reaction, contents in the reactor is distilled and separated into biphenyls, solvents and Pd/C catalysts in solvents. Pd/C catalysts in solvents are reused for the next reaction. Solvents are reused at the solvent showering tower. Biphenyls and hydro-chloric acid are shipped outside facility to be recycled, after clearing PCB elimination tests (Ohno, Yagi, Ohbayashi and Saitoh, 2007).

3. Treatment Process of the plant

The total process consists of 3 major batch system technologies:

A. Cleaning;
B. Vacuum Thermal Extraction and Recycling: Collection of PCB for separating from electric equipment by thermal treatment under vacuum
C. Decomposition system by Catalytic Hydro-Dechlorination (already described before and process scheme follows)

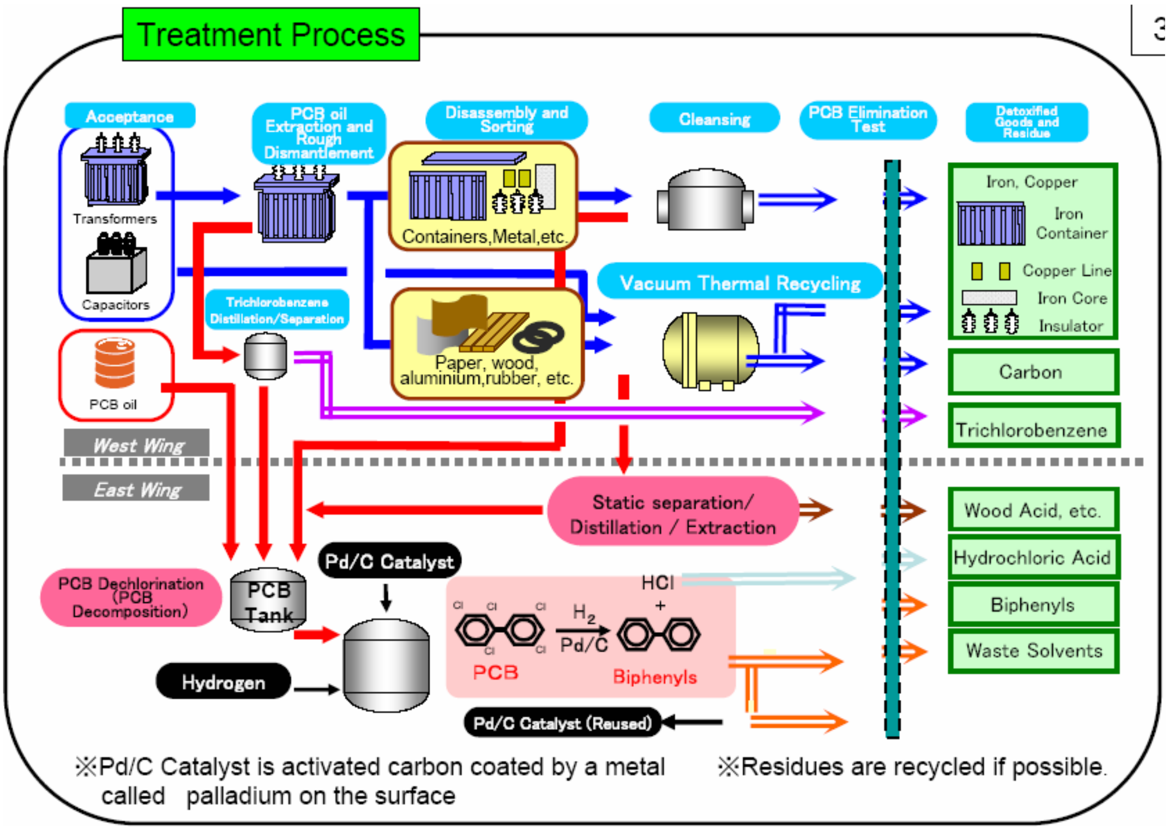

Figure 3: Overview of total treatment process of the OSAKA plant

Process	Outline
Acceptance	• PCB wastes are accepted in the daytime, and stored temporarily indoors.
PCB Oil Extraction and Rough Cleansing	• PCB oil is extracted from transformers and large capacitors, and the internal parts are roughly cleansed.
TCB Distillation/Separation	• Extracted PCB oil is separated into PCB and TCB inside the distillation tower.
Disassembly and Sorting	• To make cleansing of the internal parts easy, containers are disassembled and sorted by material.
Cleansing	• Containers and inside metal parts are cleansed to remove PCB.
Vacuum Heating	• PCB contained in capacitors and impregnated materials such as PCB soaked paper and wood are heated in vacuum, separated and collected by oil scrubbers.
Leave at rest / Distillation / Extraction	• PCB and wood acids separated in the vacuum heating furnace are left at rest, distilled and extracted.
Dechlorination (PCB decomposition)	• PCB is decomposed by reacting chlorine with hydrogen in the presence of Palladium Carbon (Pd/C) Catalyst.
PCB Elimination Test	• Treated materials are tested if PCB is eliminated. Only material that have cleared legal standards are shipped outside of the facility.

Table 1: Schematic overview of individual process steps

Figure 4: Overview of individual process steps

Ad A. Cleaning

Details of Cleaning System:

Cleaning system means a treatment for removal of PCB from the electric equipments such as transformers and large capacitors. Though PCB is extracted with a pump from the equipments, much PCB remains inside of them. In order to remove PCB completely, equipments are cut to the suitable size and washed with solvents. Solvents used for washing are distilled and reused. Metal parts of equipments are easily cleaned, however, paper and wood contained PCB are difficult to be removed PCB by washing, and are treated by thermal treatment under vacuum (VTR).

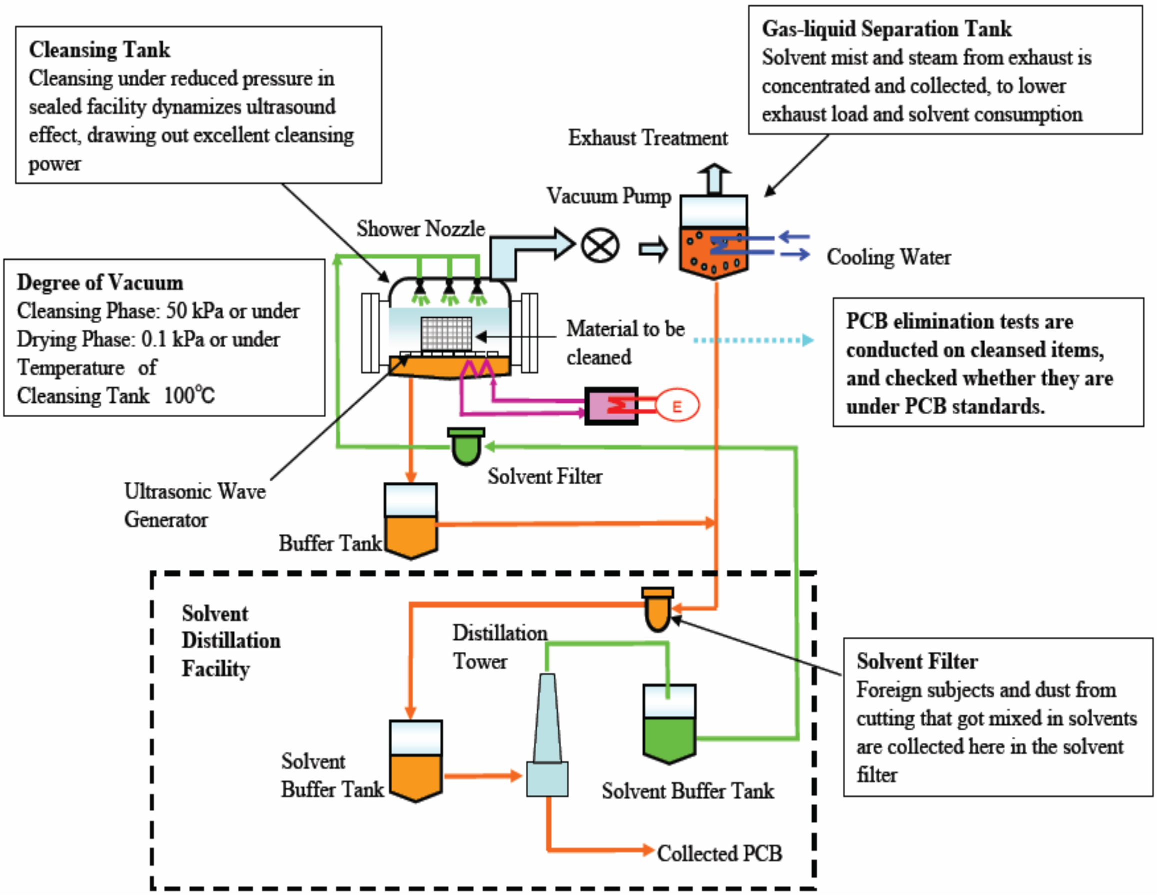

Figure 4: Overview of Cleaning Scheme

Ad B. Vacuum Thermal Extraction and Recycling (VTR)

Process Scheme
In the vacuum furnace the material is heated up to a certain temperature until the PCB oil is evaporated. The PCB gas is lead to a special off-gas system to condense all the PCB vapors back to PCB liquids and collect them inside the closed vacuum tank.

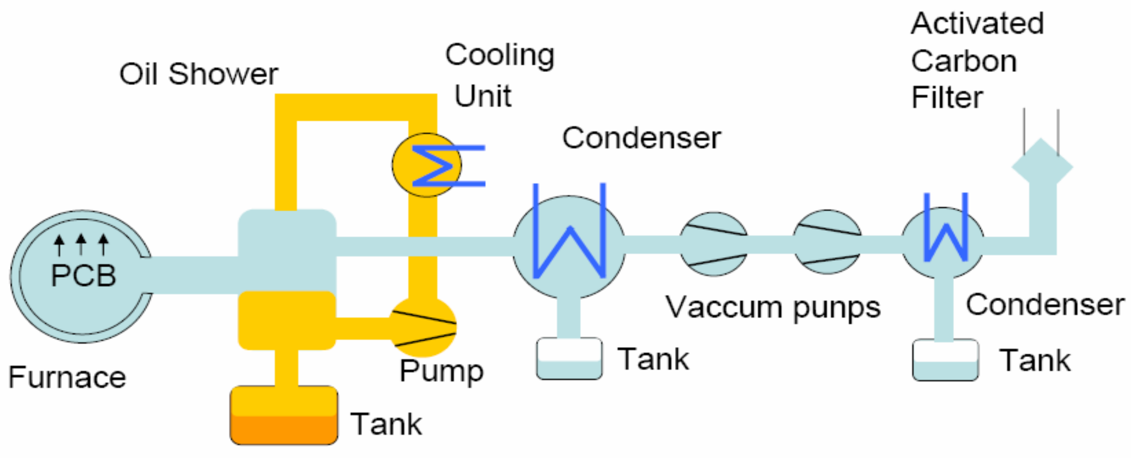

Figure 5: Process Scheme of Extraction and VTR

Ad C. Details of Decomposition system by Catalytic Hydro-Dechlorination

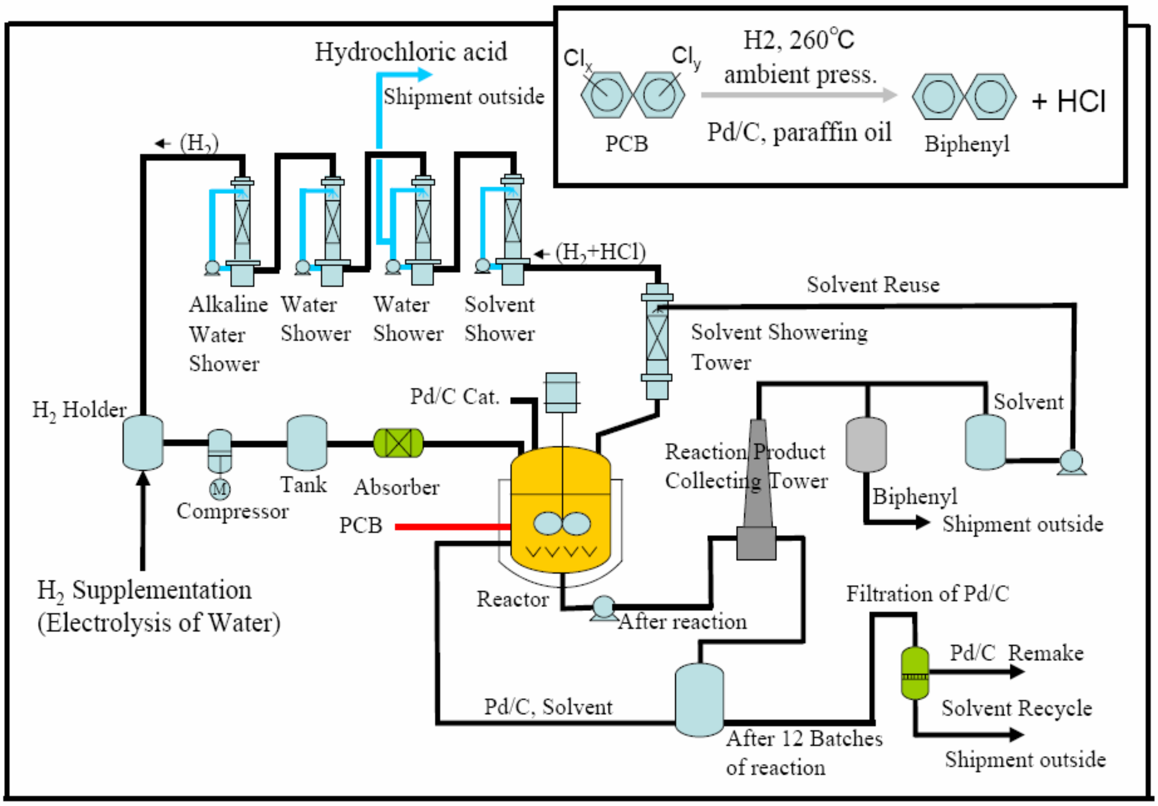

Figure 6: Process scheme of CHD System

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PART I: Criteria on the Adaptation of the Technology to the Country

A. Performance:

1. Minimum pre-treatment:
For the PCB oil no pre-treatment is needed.

Pre-treatment is needed for transformers and capacitors. Oil will be extracted from the transformers and large capacitors and the internal parts are roughly cleansed. Extracted PCB oil is separated into PCB and TCB inside the distillation tower. To make cleansing of the internal parts easy, containers are disassembled and sorted by material. Containers and inside metal parts are cleansed to remove PCB. PCB contained in capacitors and impregnated materials such as PCB soaked paper and wood are heated in vacuum, separated and collected by oil scrubbers. PCB and wood acids separated in the vacuum heating furnace are left at rest, distilled and extracted. Treated materials such as iron containers, copper wires, iron cores and insulators are tested if PCB is eliminated. Only material that have cleared legal standards are shipped outside of the facility and go for recycling.

2. Destruction efficiency (DE):
Table 2 shows the results of the batch reactions with 2L glass vessel.
Figure 7 shows the experimental apparatus.

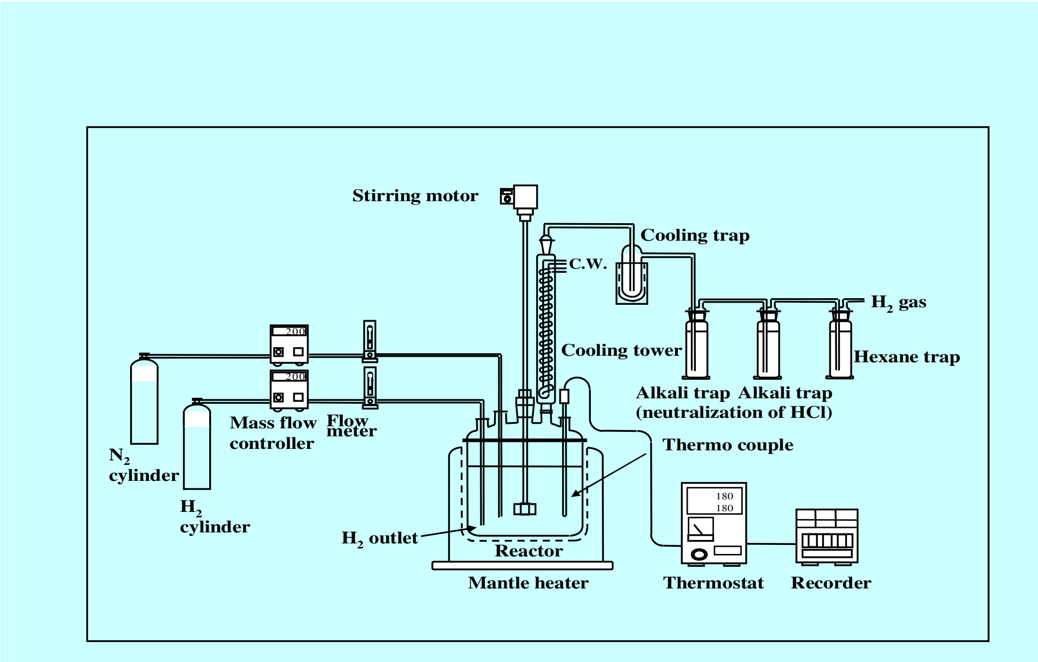

Figure 7: Experimental apparatus by catalytic hydro-dechlorination (C.H.D.)

	PCB	PCB (ng/g)		DE (%)	Dioxin(ng/g)		DE (%)
		Before Reaction	After Reaction		Before Reaction	After Reaction	
1	KC-500	86,000,000	860	99.999	12,000,000	1.9	99.99998
2	KC-500	68,000,000	3,500	99.995	10,000,000	1.6	99.99998
3	KC-400	71,000,000	1,300	99.998	4,600,000	1.6	99.99996
4	KC-300	81,000,000	550	99.9993	2,000,000	8.7	99.9996

Reaction time: 240 min, Reaction Temp.:240 ℃

Table 2: Results of the batch reaction of PCB

DE:99.995～99.9993 (at batch reaction for PCB)

In the OSAKA PCB Waste Treatment Facility, it is difficult to calculate DE because PCB is injected continuously for 1 hour to the reactor, then the initial PCB concentration is not decided. When the initial PCB is defined to the concentration of the liquid be injected to the reactor, DE can be calculated.

	PCB (mg/kg)		DE(%)
	Initial	After reaction	
1	98,000	0.21	99.9998
2	120,000	0.27	99.9998
3	100,000	0.14	99.9999
4	54,000	0.19	99.9996

Table 3: shows the examples of results for test reaction in OSAKA facility.

52 batches of test reaction had been done before commercial operation started in autumn 2006. (DE:99.9996～99.9999)

3. Toxic by-products:
The by-products are biphenyl and hydrochloric acid. A part of biphenyl is hydrogenated in the reaction and produces phenyl-cyclohexyl and bicycrohexyl. They are reused as fuel oil. Hydrochloric acid is reused as neutralizer.
None of toxic by-products were detected.

4. Uncontrolled releases:
Osaka PCB Waste Treatment Facility was designed with a high degree of intrinsic safety.
Vapour release pass through oil scrubber and double activated carbon filters before release.

5. Capacity to treat all POPs:

Installation is dealing with PCBs. There are no data about other POPs, however all organically bonded halogen groups must be dehalogenated.

Compounds treated:
All types PCBs have been treated on as industrial scale.
Dioxins (PCDDs/PCDFs) were dechlorinated. Dioxins, containing 1900-3700 ng/kg (39-110 ng-TEQ/g) in PCB were pulled out from the capacitors. After reaction of CHD, concentration of Dioxins decreased to ND-3.7 ng/kg (ND-0.0018 ng-TEQ/kg).

Penta-chloro-phenol (PCP) has been treated on a 200ml beaker reactor.

6. Throughput:

6.1 Quantity [tons/day, L/day]
2 t/d

6.2 POPs throughput : [POPs waste/total waste in %]
KC-300 taken from capacitors is injected directly to the reactor, then 100 % PCB can be treated. This means that 2 t/d of 100 % PCB can be treated by the plant.

7. Wastes/Residuals:

7.1 Secondary waste stream volumes:

PCBs + H_2 ⟶ Biphenyl + HCl

When 2t/day of PCBs is treated, biphenyl and HClaq (20%) is produced 1,094kg and 4,794kg respectively.

Actually, 231,095kg of PCBs was treated so far, 193.700kg of biphenyl and 617,200kg of HCl were collected and they were received by the recycling company. Biphenyl is used as fuel, HClaq is used as neutralizer.

Purity of collected biphenyl was about 60%, because biphenyl was collected with solvent by the distillation.
In the distillation, biphenyl is recovered first, and then solvent is collected.
Solvent remains in the piping of the top of the distilling apparatus.
When biphenyl is collected, the solvent is collected together.

PCBs	Amount
H18/10 ~ H19/3	19,708 kg
H19/4 ~H20/3	165,653 kg
H20/4 ~ H20/6	45,734 kg
Total	231,095 kg

Table 4: Amount of PCB treated

7.2 Off gas treatment:

In the reaction there is no off gas, however, gradually hydrogen gas in the reactor is polluted by the by-product of the tar come from VTR process, then a part of hydrogen gas in the reactor is discharged and fresh gas is charged.
Pd/C plants are equipped with active carbon traps in preparation for the discharge of the hydrogen gas.

7.3 Complete elimination:

Detailed information and treatment examples:
See Annexes:

Table 1: Technology Overview – Summary Technical Details
Table 2: Overview Project Experience per Technology Supplier
Table 3: Overview detailed project information per project – Project name (from Table 2):

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PART II: Criteria on the Adaptation of the Country to the Technology

Note: This part has to be filled in every time the "suitability" of the technology has to be examined for a certain country situation!!

A. Resource needs:

1. Power requirements :
38,000kwh/day

2. Water requirements:
30m³/day (cooling water)

3. Fuel volumes:
Fuel gas 9000Nm^3/day

4. Reagents volumes:
For every batch of reaction, 2250kg of paraffin oil, as the reaction solvent, and 10.625kg of catalyst is required. (10.625kg is the average of 12 batches. For the first batch, 34kg of catalyst is needed; 8.5kg of catalyst is added at from second batch to 12th batch. When the 12th batch is finished, catalyst is recovered.)

5. Weather tight buildings:
The Process itself has no special requirements other than rain shelter.

6. Hazardous waste personnel requirement:

7. Sampling requirements/facilities:

8. Peer sampling:

9. Laboratory requirements:

On site requirements:
Reaction temperature, flow volume of H_2 and revolutions of the stirring in the reaction vessel are controlled.
Requirements in country:
Many requirements are described in the "Guide Book for PCBs Treatment Technology (2005) (in Japanese)"
For example, the material of the floor in the facility should be impermeable.

10. Communication systems:
By means of remote control, the reaction system is managed from a control room but the sampling of the reaction liquid takes place from the reactor. Data of temperature, pressure volume and so on, is stored in PCs.
Mobile network:

Fixed network:
Standard telecommunication facilities.

11. Number of personnel required:
16 people in total are working at the PCB degradation facilities. （About 80 people are working at the pre-treatment of parts, for example acceptance, disassembly and sorting, cleansing and VTR treatment). 12 people are divided into 4 groups, and are working in shifts. 4 people are working during the day time.

11.1 Number of Technicians required (skilled labour):
4 group leaders of 4 shift groups must know the details of the process and how to run the DSC system. In the Osaka PCB Facility, 4 people of these started education and training 6 months before start of the test runs.
2 people working in the day time must know well about facility like 4 group leaders.

11.2 Number of Labourers required (unskilled labour):
16(total workers)-4(group leaders)-2(day time workers)=10
10 workers are unskilled labours.

B. Costs: (100 yen = 0,95 US, at Sept 2008 exchange rate)
Charges for treatment of the capacitors and transformers have been decided by JESCO:
For example, 10~15 kg of capacitor cost 472,000 yen (4484 US$), 200~215 kg of capacitor cost 1,911,000 yen (18154,5 US$). Small companies can get the support from the Japanese government for the treatment costs. Small companies only have to pay 25% of the charge.
The cost of the equipment has been established according to the total weight. In the case of PCB oil only, the cost has been established 3,250 yen/ L-PCB oil.

There is no breakdown of the costs possible. Therefore the below listed costs are not filled in

1. Installation and commissioning costs [US Dollars]:

2. Site preparation costs [US Dollars]:

3. Energy & Telecom installation costs:

4. Monitoring costs:

5. Complying costs:

6. Reporting costs:

7. Running costs with no waste:

8. running costs with waste:

9. Decommissioning costs:

10. Landfill costs:

11. Transport costs of residues:

C. Impact:

1. Discharges to air:
160m³ of hydrogen gas are discharged to air per day in the case of full load (8 batches in a day)

2. Discharges to water:
None

3. Discharges to land:
None

4. Soil impact (noise etc):
None

D. Risks

1. Risks of reagents applied:
Paraffin oil: No risk but can burn
Hydrogen gas : No risk but explosion
In the Osaka PCB facility, over 50 sensors of H_2 are situated in the space of the reaction section. When over 2 sensors perceives H_2 gas, facility urgent stops automatically.

2. Risks of technology:
Risks associated with operation is low because reaction condition is mild (260℃、normal pressure), and the heat of reaction is small, so the reaction does not progress without permission.

3. Operational risks:
Heating and pressure control are fully automatic and intrinsically safe. A lot of sensors for H_2, oil, fire, water, temperature, are situated at the suitable place in the facility.

E. Constructability:
Facility has no special materials and equipments.

1. Ease of installation/construction of plant:

2. Ease of shipping/transit:

3. Ease of operation:

4. Ease of processing :

F. Output/generation waste:

1. Generated waste (% of input waste)
Iron, copper, carbon, trichlorobenzene, wood acid, hydrochloric acid, biphenyl and waste solvents are the generated materials. However, most of them are recycled, then the amounts of waste are very small.
When the facility treats only PCB oil, no waste is generated.

2. Deposited waste at landfill (% of input waste)
Ceramic insulator is the only material to deposit at landfill, but the weight of the total input of capacitors and transformers is not known exactly.

3. Waste quality properties (pH, TCLP)

**Note: This Technology Specification and Data Sheet (TSDS) does not certify any particular technology, but tries to summarise the state of the art of the concerned technology on the basis of data delivered by the companies or other sources, which have been made available to the author and refers the reader to original documents for further evaluation. Without the efforts below listed technology suppliers it would not have been possible to set up this TSDS. Date 11.11.2008*

Technology suppliers that have contributed to this TSDS: :

Masayuki Ohno, Kanden Engineering Corporation
Dr. Yukio Noma, National Institute for Environmental Studies, Japan

References:

1) Ohno M. and Hirata K.; *Complete Destruction of PCB by Using A Catalytic Hydrogenation-Dechlorination Reaction and t-BuOK Method in A Bench Scale Plant*, ORGANOHALOGEN COMPOUNDS, Vol.31, 405-409 (1997)

2) Noma Y., Muramatu T., Nishizawa K., Ohno M. and Sakai S.,; *Dechlorination Pathways of PCBs by Photochemical Reaction and Catalytic Hydro-Dechlorination*, ORGANOHALOGEN COMPOUNDS, Vol.56, 413-4416 (2002)

3) Noma Y., Ohno M. and Sakai S.; *Pathways for The Degradation of PCBs by Palladium-Catalyzed Dechlorination*, Fresenius Environmental Bulletin, Vol.12-No 2b, 1-7, (2003)

4) Takigami H., Ohno M., Ohara A., Shiozaki K., P. A. Behnisch and Sakai S.; *Practical Calux-Monitoring of PCB Wastes During Their Chemical Dechlorination Treatment*, 23rd International Symposium on Halogenated Environmental Organic Pollutants and POPs, Volume 1, Section 3, ORGANOHALOGEN COMPOUNDS, Vol.60-65, Dioxin 2003 Boston, MA (CD-ROM)

5) Noma Y., Muramatu T., Ohno M. and Sakai S.; *Dechlorination Pathways and Kinetics in Photo-Chemical Reaction and Catalytic Hydro-Dechlorination*, 23rd International Symposium on Halogenated Environmental Organic Pollutants and POPs, Volume 4, Section 2, ORGANOHALOGEN COMPOUNDS, Vol.60-65, Dioxin 2003 Boston, MA (CD-ROM)

6) Sakai S., P. A. Behnisch, Hosoe K., Shiozaki K., Ohno M. and A. Brouwer,; PCB Destruction by Catalytic Hydrodechlorination (CHD) and t-BuOK Method, ORGANOHALOGEN COMPOUNDS, Vol.54, 293-296 (2001)

7) Ohno M., Yagi F., Ohbayashi H. and Saitoh S.; Performance of the PCB Waste Treatment Facility for Recycling of PCB Containing Transformers and Capacitors, in JESCO/Osaka JAPAN, 27th International Symposium on Halogenated Environmental Organic Pollutants and POPs, Volume , Section , ORGANOHALOGEN COMPOUNDS, Vol. 69, 2516-2519 (2007)

＊ "Decomposition of PCB by Catalytic Hydro-Dechlorination (CHD) in Osaka PCB waste Treatment Facility" (This is not published)

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