Vacuum-Thermal Recycling of Used Nickel-Cadmium Batteries

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Abstract

The Vacuum-Thermal-Recycling Process (VTR) of Accurec is the first ultra-low emission plant for Ni and Cd containing batteries to be successfully developed and installed. The economical features of this innovative process include simplification of process steps, energy savings and reduced man-power for operation. The VTR-recycling plant is made up of small recycling-devices and can be installed modular with capacities of between 500 and 5,000 t/y. Considering that traditional recycling plants need for example gas and water purification systems and pyrolysis steps, the VTR-system is most economic and cost-efficient even for small plants. Thus a possibility is created to construct flexible, cost reducing recycling plants in accordance with the situation of today's market. This was the original idea of the Basel agreement.

1 Introduction

In today's world, batteries support our every day life. Wherever we use electric or electronic equipment, batteries play a crucial role in technical terms. For the major share of batteries, the lead acid accumulators for automotive use, the collection and recycling after the end of life period is solved in an environmental acceptable way since years. In contrast, primary and secondary batteries for consumer applications usually are disposed off after their use.

Beginning 1988, environment social groups as well as battery industry took their product responsibility and started a collection scheme for batteries, containing hazardous substances like mercury and cadmium in Germany [1]. Therefore, it was obvious that a recycling facility would be necessary in the medium term future.

ACCUREC is a medium sized company, founded in 1995 with the aim of installing a recycling plant for used Nickel-Cadmium-Batteries. Based on initial concepts of the IME, Institut für Metallurgische Prozeßtechnik und Metallrecycling of University of Aachen, a vacuum-thermal-recycling process was developed in a three-year lasting period. The pilot plant was put into operation in Mülheim/Ruhr with an initial capacity of 500 t/year. After optimising and expanding, the facility reached recently a sorting and recycling capacity for 2500 t of consumer batteries a year [2]. In 1998 ALD Vacuum Technologies AG became the major shareholder of ACCUREC. ALD is one of the world leader in the field of design and manufacture of vacuum systems for metallurgical processes and vacuum heat-treating and obtains with 300 engineers a revenue of 180 million DM a year. Looking for new activities, ALD now develops with cooperating companies like ACCUREC a zero-emission treatment concept for various recycling applications.

2 Battery recycling: a future market

Batteries as storage of energy for consumer items play an important role in the economy. However, after their use the problem arises of how to dispose of them. Every year around 160,000 to 200,000 t of small primary and rechargeable batteries are sold to European consumer market. Thus a considerable amount of tonnages containing harmful heavy metals increases emissions of incineration plants and disposal sites [3].

2.1 Background of legislation

Opposed to small consumer batteries, the existing collection and recycling system for the widely used lead-acid batteries, mainly coming from automotive application, is working well, reaching an overall recycling rate above 95 %. The reason for this considerable result is, that there was always a positive economic value for a lead-acid battery scrap, existing collection systems and recycling plants. Unfortunately more than 80 % of used consumer cells are zinc containing primary batteries. Their metal value is not sufficient to cover the recycling costs. Therefore the targeted collection of consumer cells needs a legislative base and motivated the European commission to set up several directives [4].

Directive 91/157 on batteries containing dangerous substances

- Ban on primary batteries containing > 0.05 %Hg
- Batteries are hazardous waste if they contain:
  > 0.25 mg Hg per battery
  > 0.025 % Hg or Cd in batteries
  > 0.4% Pb
- and have to be collected separately.

Directive 93/86

- Batteries concerned by Directive 91/157 have to be marked in order to inform consumer, that these batteries do not belong to normal household waste.

Directive 98/101

- Ban on batteries containing more than 0.0005 % Hg.

Although these directives lead to the same obligation on all EU-countries, the variety of national implementations is wide. Whereas it has no practical effect in 50 % of the European countries, some others like Sweden, Denmark or the Netherlands put in force some more strict regulations, collection- and refund systems.

Concerning Germany, which is the major user of small consumer cells in Europe, a voluntary agreement between battery industry and the association of trade business was already introduced in the early 90's, starting a collection program, focused on Nickel-Cadmium- and Mercury-Batteries.

Due to an insufficient collection result, the parliament set in force a battery ordinance on October 1998, which fully applied all EU-directives to national law. It states:

- that the consumer has a duty to collect used batteries separately after their end of life
- batteries are collected country-wide through the channel of retailer shops and municipalities - free of charge
- battery industry has to organize and to finance the collection and recycling

Based on the experience that usually the consumer is not educated enough to distinguish between batteries with and without hazardous substances, the legislator decided to collect all kind of battery-types, in order to increase the collection-efficiency.

2.2 Nickel-Cadmium-Batteries: market data

The Nickel-Cadmium Battery, invented in the beginning of 19th century, is the most successful rechargeable battery system beside lead-acid batteries. It is providing the double power density in comparison with lead-acid and has a high reliability in hot or cold regions, where lead-acid is not applicable. Two major types were developed:

- the vented cell with application for back up power systems, emergency lighting, power storage for engine starter or electrical vehicle (ELV)
- the sealed cell for professional and consumer used cordless tools, mobile communications, home appliances or individual emergency lightings

10 years ago the largest market growth for vented NiCad-cells was estimated for ELV. Because of today's knowledge, there will be no commercial and competitive use of ELV's in the near future, so that this market stabilized at 3,000 t/y in EU.

A considerable market growth for sealed cells was indicated in the beginning of the 80's. Shown by table 1, mainly caused by new applications for telecommunications, electric and electronic equipment (EEE), the sales of small rechargeable NiCad-batteries increased 400 % until 1995 [5]. Due to the fact that especially in the segment of telecommunication and computer, industry looked for new battery systems with low weight and high power density, alternative rechargeable systems like Nickel-Metal-Hydride or Lithium-Ion-Accumulators, were invented and introduced into the market. As a result NiCad-batteries were replaced in the segment of EEE partially. However, the booming market of power tools for professional and consumer use lead to an overall increase of NiCad-sales until today.

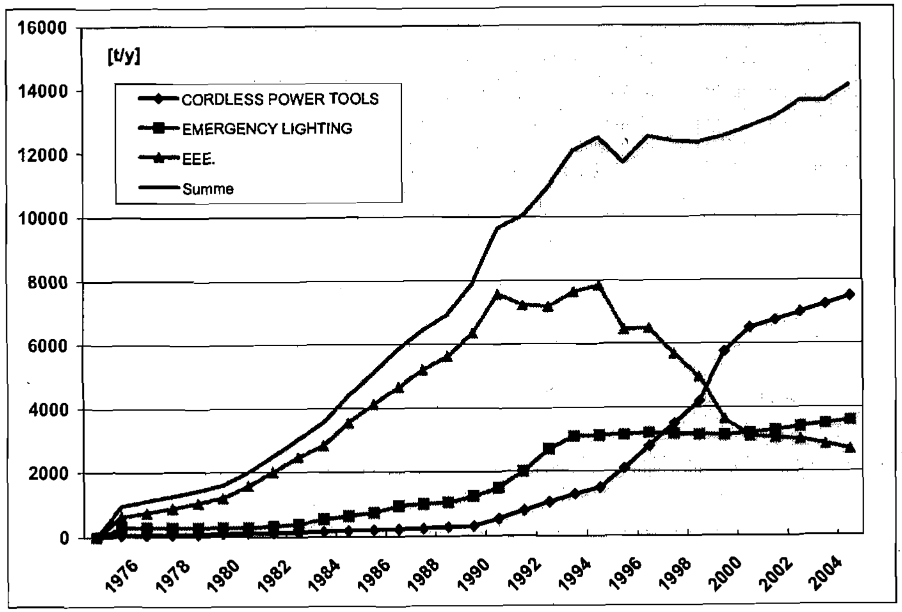

Figure 1: NiCad-Battery Sales in EU

Depending on the application and using habits of the customer, batteries reach their end of life after 1½ to 7 years. Taking into account additionally that an end user holds back and hoards these batteries some time, the theoretical amount of discarded batteries could be estimated. Around 8,500 t of NiCad-accumulators were supposed for the waste stream in 1999. Table 1 compares these data with the practical collection and recycling results over the last years in Europe. Although there is an average growth of recycled sealed NiCad's of 33 % every year, the total recycling rate in 1999 was only 17 %. Considering the ongoing, ambitious efforts in terms of battery collection, the demand of further recycling capacities for the future is obvious.

Table 1: Collection and Recycling of NiCad-Batteries in EU

	[t] 1994	[t] 1995	[t] 1996	[t] 1997	[t] 1998	[t] 1999	Inhabitants [Mio.]	g NiCad/inhabitant in 1999
Austria		31				51	8,1	6.3
Belgium	9	10	10	50	66	59	10.1	5.8
[illegible]			9	44	55	65	5.3	12.3
[illegible]		1	6		12	5	5.1	1.0
[illegible]	60	35	70	105	92	144	60	2.4
[illegible]	220	206	303	440	403	596	82	7.2
[illegible]							11	0.0
[illegible]	1			2	1	25	57	0.4
[illegible]	10	29	35	75	107	135	16	8.4
[illegible]		2	10			12	4.4	2.7
[illegible]							9.9	0.0
[illegible]		4			1	38	39	1.0
[illegible]		108	110	142	143	169	8.7	19.4
[illegible]	18	63	72	94	46	75	61	1.2
[illegible]	34	96	46	21	144	168	7,2	23.3
[illegible]	352	585	671	973	1040	1430	388	3.7

3 Status of Consumer-Battery Recycling

The battery types introduced into the market and collected after their end of life can be divided into:

- zinc-containing batteries (Zinc-Carbon / Alkaline-Manganese)
- Mercury containing batteries (Hg-button cell)
- Lithium-containing batteries (Li-Manganese dioxide / Li-Ion)
- Nickel-containing batteries (NiCad / NiMH)

Although Zn-C and Al-Mn batteries take the majority of battery types with more than 80 %, there is no recycling plant available yet. Due to a still high Hg-content in the mixture of collected primary batteries and the low metal value, industry fears an uneconomic costly recycling. A dumping of those batteries is still their prefered solution. For the decreasing share of high mercury containing batteries, there is a European-wide network of recycling facilities since years [6]. For the modern Li-system, there is no established recycling technology available until now.

In the past, Nickel-Cadmium batteries were recycled mainly in two facilities abroad. The technology of both companies is based on a similar atmospheric distillation process [7].

Vented NiCad-cells are drained and de-assembled mechanically into Cd-containing (negative plate) and Cd-free parts (positive nickel-plate and cases). The negative plate can be charged to the Cd-distillation furnace directly. Sealed cells have to be treated first 12h in a pyrolysation furnace at 350 °C. Water and organics are evaporated and combusted in an afterburner. The resulting waste gases are cleaned finally in different absorption filters.

Pretreated sealed cells are deloaded, transported and charged together with negative plates again with addition of reduction coale to steel baskets. They are stapled on a water-cooled steel condenser-plate up to a weight of 1 t, which has a center hole where liquids can drop through. For protection against atmosphere, these baskets are covered with a steel hood against the atmosphere and sealed with ceramic powder, before the heating hood is put in place. Up to 1,000 °C, this distillation furnace heats and reduces the CdO in order to evaporate Cd-metal in a 24 h lasting process. Cd-vapour can condense at the bottom and is collected below the center hole. There, process-gases and Cd-dust are also evacuated and cleaned in connected filters. After an 8 h cooling period the remaining Ni-Fe-scrap with a rest of 0.1–0.5 % Cd can be unloaded and sold. Both facilities are working since the beginning 80's and represent today a recycling capacity of 5,000 t of NiCad-battery scrap together.

Judging this traditional process technology, some major features have to be mentioned:

- Low investment costs due to simple technology
- High wear costs and maintainance
- High running costs for air and water cleaning systems
- High personnel costs due to fact that a running process has to be supervised around the clock
- Probability of sealing rupture and contamination of environment and human life
- Working area around the distillation furnaces is highly contaminated with Cd and CdO.
- Employees have to be protected passively during working shift.

Some of these obvious technical disadvantages of the conventional technology and one of the most strict legislations with regard to the environment and permission procedures motivated to develop and install an innovative recycling technology.

4 Vacuum Thermal Treatment for Recycling Applications

The idea of an innovative recycling plant was based on the following considerations:

- the process should dramatically decrease emissions in order to comply with the strict regulations
- offer cost-effective production by means of automation and rationalization of the work processes

- provide a maximum protection during processing and handling harmful substances like heavy metals.

These objectives led to the use of vacuum and the development of the VTR process:

Vacuum Thermal Recycling.

This **VTR** process makes use of the advantages of the vacuum because

a) in the vacuum all elements evaporate at a significantly lower temperature. This results in saving of energy and material use.

Table 2: Evaporation-temperatures

Pressure [mbar]	1000	100	10	1	0.1
Mercury vaporizing at °C	357	245	174	116	71
Cadmium vaporizing at °C	767	588	458	374	310
Zinc vaporizing at °C	907	709	574	471	394

b) the hermetic construction prevents the contamination of gases by heavy metals. Costly treatment of waste gases can hence be avoided.

5 Recycling of Nickel-Cadmium-Accumulators

Regarding the recycling of NiCad-batteries the VTR-concept was adapted to the ACCUREC process. ACCUREC recycles both NiCad-types:

- **Vented NiCad**-accumulators

After initial removing packaging and connecting pieces, the batteries are drained from electrolyte, which after filtration can be used in a process to abstract tin. In several semi-automatic dismantling machines the accumulators cases are separated. Battery parts containing cadmium are submitted to the VTR process for distillation of heavy metal. The remained Cadmium-free nickel scrap is used as secondary Ni-derivative in the steel industry.

- **Sealed NiCad-accumulators**

Consumer accumulators are initially sorted according to packs and single cells. The plastic is removed mechanically from the battery packs, so that the remaining batteries together with the single cells can immediately be directed to the VTR-process without further treatment. This simplification illustrates the innovation of this process. The treatment step of pyrolysis, needed in traditional recycling systems is not required. In addition the cost-intensive exhaust gas purification station is completely unnecessary and obviated.

The VTR **construction** is basically made up of vacuum-sealed hot and cold zones, vacuum pumps, the heating device and control unit. The furnace is constructed from a quartz pipe into which the charging container, holding at least 0.7 t batteries is inserted by crane. The quartz pipe is vacuum-sealed with a stainless steel lid at the top, whereas a water-cooled condenser is connected at the bottom-side. A two stage pump station can create a vacuum of 1.0 mbars.

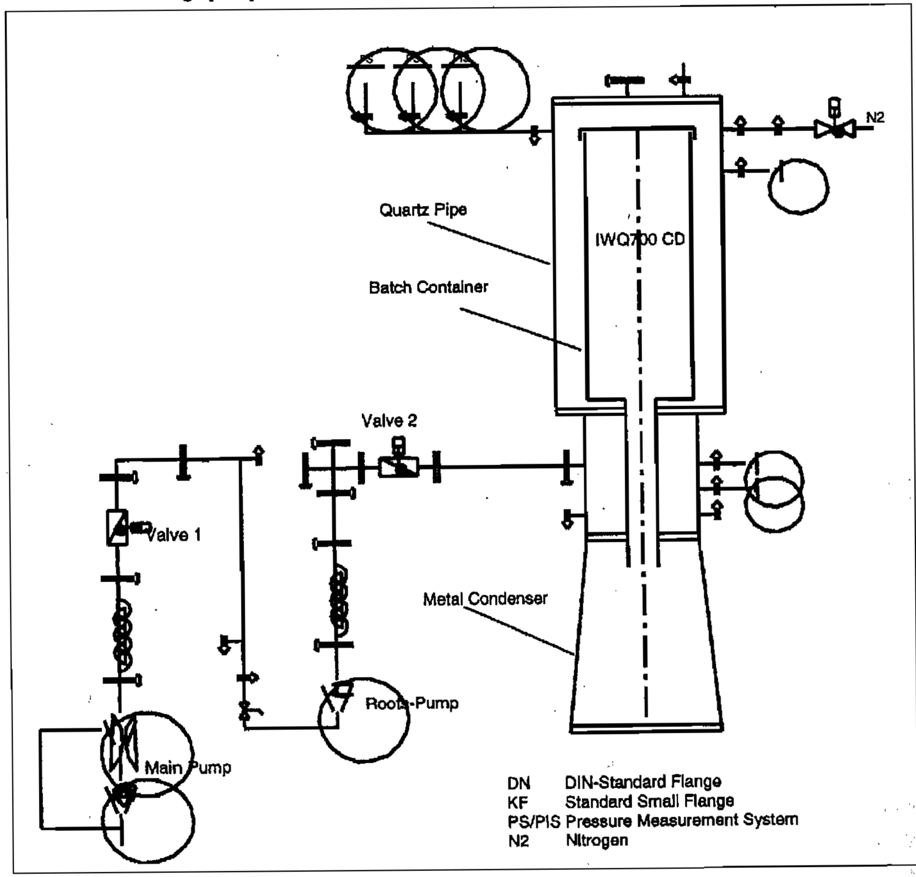

Figure 2: Schematic Design of the Vacuum-Recycling Furnace

An induction coil surrounding the quartz pipe heats the batteries without contact to an initial temperature of 300-500 °C. After the water and organics are evaporated the charge can be heated up to the operating temperature of max. 850 °C within about one hour. Mainly in this treatment period, the following chemical reactions (R1-6) occur:

$$Cd(OH)_2 \leftrightarrow CdO + H_2O \quad \text{(R1)}$$

$$CdO \leftrightarrow Cd + 0{,}5\,O_2 \quad \text{(R2)}$$

$$CdO + C \leftrightarrow Cd + CO \quad \text{(R3)}$$

$$CdO + CO \leftrightarrow Cd + CO_2 \quad \text{(R4)}$$

$$2\,CdO + C \leftrightarrow 2\,Cd + CO_2 \quad \text{(R5)}$$

$$2\,CO + O_2 \leftrightarrow 2\,CO_2 \quad \text{(R6)}$$

The reduced CdO is now evaporated and streams through the central steam-pipe down to the condenser. The metal vapor generally finds its way to the coldest area, here the water-cooled metal-condenser at the bottom, where it forms a metallic cadmium block. After approx. 5 hours' treatment in this last stationary position the process is complete.

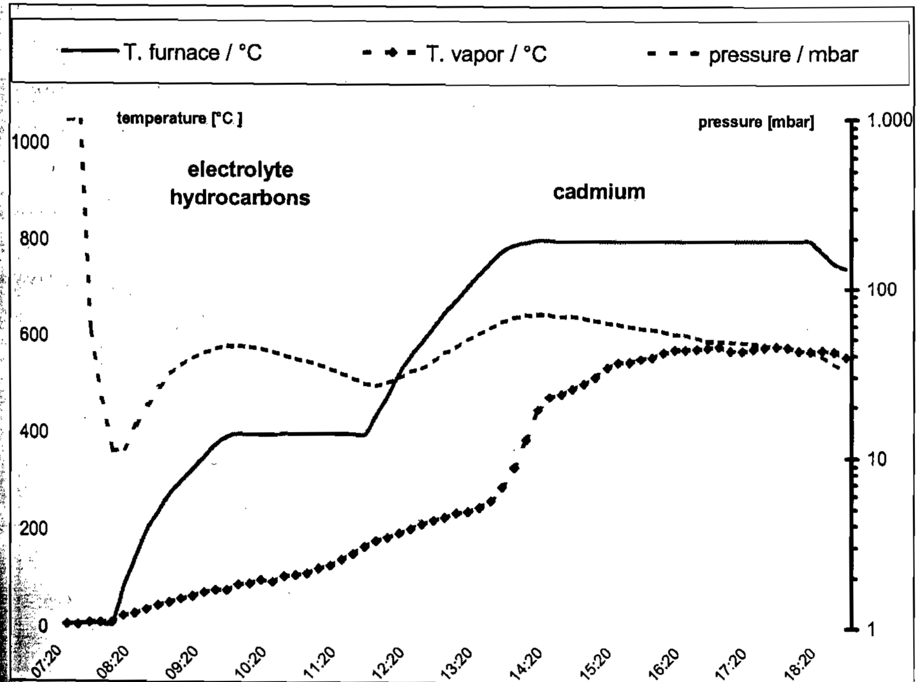

Figure 3: Temperature and Pressure while Treatment of spent NiCad-Batteries

The main **commercial product**, an iron product with a high nickel content now remains in the charging container. It contains 50-250 ppm of rest-cadmium, and is an approved scrap for alloy stainless steel production. The cadmium metal that has been distilled in one step is obtained in a form, which can be immediately reintroduced into the electrolytic battery manufacturing process or oxide production. Table 3 shows a representative analysis.

Table 3: Impurities of recycled cadmium

Element	Cr	Zn	Pb	Others
[mg/kg]	< 0.5	15	12	< 150

Since pure NiCad-battery batches, without parts of other battery types, are loaded and treated, it is possible to guarantee a 99.95 % pure cadmium content. Additionally, both product qualities are continuously monitored by a X-Ray lab.

Regular control measures by authorities and independent environmental institutes have confirmed the **ultra-low emission** status of the process. Careful handling of heavy metal products and the absence of exhaust gases containing cadmium mean that the work place remains extremely safe.

Table 4: Air pollution measurements at main working stations of the recycling facility

Station	De-assembling	Thermal Reactor '97	Thermal Reactor '98	Mercury
[µg/m³]	Cd 2.4	Cd 3.5	Cd 1.8	< 0.05

Thanks to an intensive analysis of the exhaust gases resulting from the process, continuous checking of the exhaust is no longer necessary. During the thermal treatment the process emits, depending on input products, only 100-1,000 l/h of exhaust gases at most. A typical composition of this exhaust gas is illustrated in table 5. It is composed only of carbon monoxide and carbon dioxide. Other pollutants cannot be measured. Nevertheless an additional active carbon filter has been connected. Further requirements and expenses for exhaust gas or wastewater cleaning are prevented.

Table 5: Exhaust gas contaminations

	CO_2	CO	Cd	Hg	Dioxins
[g/h]	58	4	n.m.	n.m.	n.m.

n.m. Not measurable

Figure 4: Products: Cadmium balls and Ni-Fe-scrap

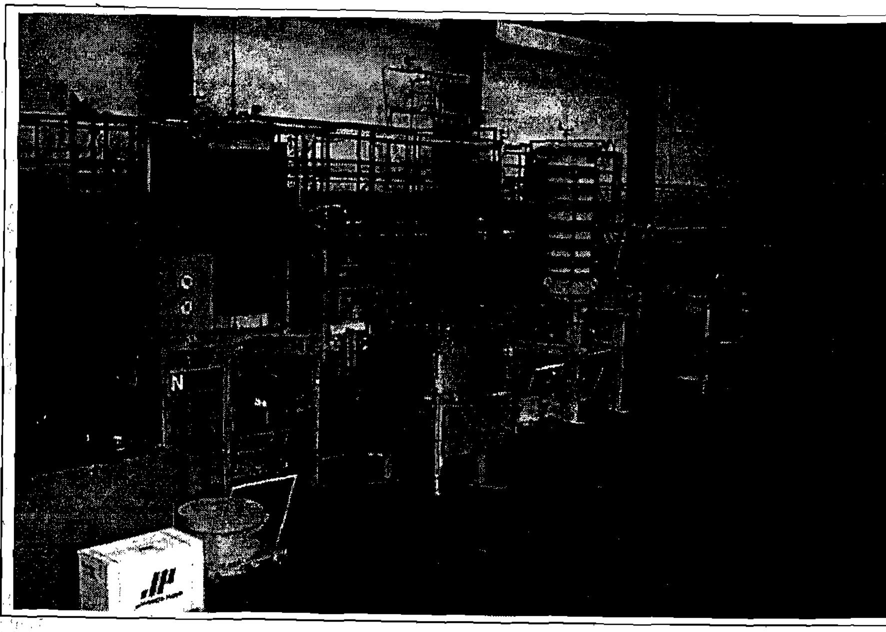

Figure 5: Partial view on Battery Recycling Furnaces at ACCUREC® / Mülheim

6 Summary and outlook

In this environmentally friendly way 3,000 t/y NiCad batteries have already been recycled at the ACCUREC plant in Mülheim. Since 1997 3 Million DM were invested to develop, install and expend a NiCad-battery recycling plant to its final capacity of 2,500 t/y with beginning of the year 2001.

With the innovative **VTR** process of ACCUREC and ALD, the first ultra-low emission plant successfully unites the *economic* and *ecological* features:

- Reduction in necessary steps in the treatment
- Energy saving because of significant lower temperatures and shorter treatment time
- Savings on costly purification plants for waste gases and water
- Reduction in staff due to increased automation
- Reduction of emission as far as it is technically possible
- Avoidance of staff exposure to emissions

This technology generally is also applicable for further recyclable products. Several mercury-recycling plants were already delivered in the last 5 years. VTR-furnaces for special metal-alloy-recycling, electronic waste as well as de-contamination of hazardous materials e.g. PCB-transformers were developed and can be delivered.

The **VTR** recycling plant is made up of small recycling-devices and can be installed modular by between 500 and 5,000 t/y. Considering that traditional recycling plants need for example gas purification systems and pyrolysation stations, the VTR system is economical and cost-effective even for small plants. Thus a possibility is created to construct flexible, cost-reducing recycling plants in accordance with the local market situation. This was the original idea of the Basel agreement.

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