

Don't ban PVC: Incinerate and recycle it instead!

Plastics are making a growing contribution to sustainable development. For example, over an expected lifetime of 50 years, the use of window frames and insulating materials made of plastic in buildings save many times the energy required to manufacture them. Plastics for packaging purposes provide protection against damage and dirt contamination, thereby saving considerable amounts of material and energy. Choosing appropriate disposal strategies for plastic waste also helps to protect the environment (Mark 2000).

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In many market segments there is a growing trend to PVC. For example, 54% of window frames in Germany are made of PVC. In 1997 the production of PVC in Germany increased by 9%, the fastest growth rate of all plastics. The waste stream in Germany is estimated to contain an annual total of 630,000 tonnes of PVC (calculated as pure PVC). The mixed plastic waste in municipal waste comprises 64% PE, 6% PS, 2% PET, 4% PVC and others. In the reference year 1999, recycling of PVC was more or less equally divided between substance and energetic recycling.

In their “Voluntary Commitment to Sustainable Development” of March 2000, PVC producers, converters and suppliers promised to recover some 200,000 tonnes per year of PVC waste all over Europe by 2010, in addition to the quantities already being recycled and the quantities recycled in regulated waste streams (cars, electrical and electronic scrap). In 2001 only about 8% of all PVC waste generated in Europe was recovered by substance recycling. The following recycling processes have therefore been developed and are currently being tested:

- the “Vinyloop” process,
- hydrolytic separation in a large-scale plant,
- incineration and HCl recovery in a rotary kiln,
- decomposition in a slag bath, and

- alternative fuel recovery by means of dehydrochlorination of mixed plastics for blast furnaces.
- The cost of these methods is in the region of €250 per tonne, with the exception of the Vinyloop method which is considerably lower.

The Rugenberger Damm waste incineration plant (MVR) in Hamburg offers a possible economic and ecological alternative to the aforementioned processes – incineration of PVC waste together with other municipal waste and recovery of the chlorine in the form of 30% strength hydrochloric acid. In August/September 2001 this advanced recycling technology used at the Rugenberger Damm waste incineration plant was tested in a large-scale trial involving the recovery of some 500 tonnes of foils, pipes and other PVC waste.

The European Commission has issued a Green Paper on environmental issues relating to PVC (EU Commission 2000). It examines the following aspects of interest in connection with the PVC coincineration tests at MVR:

Additives

- Quantities used, dangers and risks of additives, especially heavy metal stabilisers and plasticisers made of phthalates

- Reduction of the use of certain heavy metal stabilisers, and
Waste management
- Storage of PVC waste on landfill sites: storage behaviour,
- Recycling of PVC waste: processes and potential quantities for mechanical and chemical recycling (with input material) and other technologies.

Landfill is currently the principal disposal path used for PVC waste in many European countries. The effects of PVC constituents under landfill conditions have been and still are being discussed at EU level. Evaluation and quantification of the environmental impacts is based on the theoretical degradation rates of the PVC polymer, the release of plasticisers and stabilisers into leachates, and gases emitted to the atmosphere from the landfill site. Despite the existence of European framework conditions, the technical standard of European landfill sites display great variations. The existing technical standards with regard to basal sealing, leachate collection and control of gaseous emissions determine the environmental relevance and costs of landfill disposal. By 2020 the quantity of PVC waste requiring disposal by landfilling is expected to be around 2.8 million tonnes per year. Landfill costs are between €8 per tonne in Spain and €200 per tonne in Germany. Long-term studies of the behaviour of PVC on landfill sites have been made by a number of universities, and it has been found to be largely neutral with respect to the environment (Mersiowsky 1999). However, the imposition of a limit value for ignition loss as a condition for landfill authorisation by the EU Landfill Directive will result in a shift of priorities towards energy and substance recycling of PVC waste after it is implemented in all European countries. Recycling of PVC waste containing heavy metals can raise specific issues because of the dilution in the individual application fields that have to be mastered by closed-loop recycling systems. As things stand at present, no short-term measures are required for lead stabilisers. Extensive scientific risk assessments are in progress, with the provisional finding being that the total emissions are of minor relevance for the environment. With regard to cadmium, since 2001 the PVC industry has been implementing its voluntary undertaking not to use cadmium anymore, and for lead there is now a step-by-step reduction programme.

In addition, some 600,000 tonnes of PVC waste are incinerated in the European Community every year, mostly in domestic waste incineration plants. PVC represents about 10% of plastics incinerated and about 0.7% of the total quantity of waste disposed of by incineration. PVC waste accounts for between 38 and 66% of the chlorine in the waste streams incinerated. The other major sources of chlorine are about 17% from compostable substances and 10% from paper. In the combustion of PVC waste,

hydrochloric acid (HCl-gas) is formed in the flue gas as a result of the splitting of the main chain of polymer molecules and the consequent release of the chlorine attached to the chain. Owing to the other chlorine sources in domestic waste, it would not be possible to do without a separation stage for HCl-gas even if PVC could be eliminated.

In this connection the influence of elevated chlorine levels on the composition of the flue gas, the quality of the substance streams from a domestic waste incineration plant, the possible corrosion of the equipment in incineration plants, and the existing emission standards for incineration plants are under discussion in the EU.

Generally speaking, recycling waste as material, and above all reusing it in high-grade products, is better in ecological terms than burning it in domestic waste incineration plants or dumping it in landfills. For example, recycling PVC waste for use in high-grade building products made of PVC (window frames, pipes etc.) makes both economic and ecological sense. Coincineration of PVC in a domestic waste incineration plant is an alternative to straight substance recycling, because its thermal and chemical recovery techniques return some of the energy used for the production of PVC and also return chlorine to the substance cycle as well. However, this will undoubtedly only apply if the stringent dioxin limits of 0.1 ng/Nm^3 are implemented throughout the EU in the context of legal harmonisation and the recovery of the chlorine in the form of hydrochloric acid (as at MVR), or other chemical materials becomes a reality. In this way it can be ensured that the increase in the amount of PVC in waste does not raise the quantity of neutralisation salts from the wet flue gas cleaning processes that have to go to landfills.

The MVR plant is one of six waste incineration plants in Germany that recover hydrochloric acid from those waste components that contain chlorine. Thus these plants are an ecological and economic alternative to direct reuse of PVC as a material.

The purpose of the MVR is to combine low-cost incineration of waste with cogeneration of district heat and electricity and reusable products recovered from waste incineration or flue gas cleaning. A high standard of security, occupational safety and health, environmental compatibility and availability is assured (Schröder 2001).

In mid June 1999 the plant, designed as a CHP plant for a heat output of max. $75 \text{ MW}_{\text{thermal}}$ and a grid power input of about 3 MW, started operations. Every hour, 21.5 tonnes of waste (max. 23 t/h) is incinerated on grates in two steam generators.

Incineration is of course performed in compliance with the statutory provisions of the Federal Republic of Germany and the EU Incineration Directive at a

temperature of at least 850°C, with a residence time of 2 seconds. This results in the thermal destruction of organic components and also PVC, which is determined as a non hazardous waste so that a combustion temperature of 850°C is sufficient.

Flue gas cleaning begins in the steam generator with an SNCR system for reducing oxides of nitrogen (noxes) by injecting ammonia water into the combustion chamber, and a system to separate fly ash at high temperatures between the second and third and between the third and fourth drafts of the steam generator (Fig. 1). After the flue gas leaves the steam generator, slightly loaded active carbon from baghouse 2 is added for the adsorption of heavy metals and dioxins/furans. Residual particulates in the flue gas from the steam generator and the active carbon are separated together in baghouse 1. On its further path through the cleaning process, the flue gas passes through a two-stage acid scrubber to remove the halogen compounds, a single-stage alkali scrubber to remove sulphur oxides, and a second baghouse as a post-cleaning stage, with fresh active carbon being added to the flue gas before it enters the filter. A suction duct takes the flue gas to the stack.

The cleaned flue gases are discharged into the atmosphere via a stack 80 m high. The annual limit emission values for the MVR plant are all well below the statutory limits, and the actual measurements for the years 1999,

2000 and 2001 in turn are all well below the MVR emission limits, in some cases by several orders of magnitude. For example, the dioxin concentrations measured at the MVR stack were approximately 0.002 ng/Nm³ and thus well below the limit of 0.1 ng/Nm³.

The crude acid produced by the flue gas cleaning system is purified and concentrated in a separate HCl rectification system to produce a technical grade 30%-strength hydrochloric acid in accordance with EN 939, Type 1 (Menke 1999), which is sold to the chemical industry, the construction sector and for use in power plants. Some of it is used by MVR itself to produce feed water from river water for the boiler and for condensate cleaning.

The hydrochloric acid rectification system (Fig. 2) consists of the following components:

- Bromine-Iodine stripping with the addition of sodium hyperchlorite and absorption of these halogens by metered addition of soda lye and sodium thiosulphate
- Preliminary evaporation of crude acid with separation of hydrogen fluoride by adding aluminium chloride
- HCl distillation and preconcentration to 17%-strength hydrochloric acid
- HCl gas desorption with calcium chloride
- HCl absorption with demineralised water, adjustment to a concentration to 30%.

The residues produced during the hydrochloric acid rectification, mainly water-soluble salts, are continuously

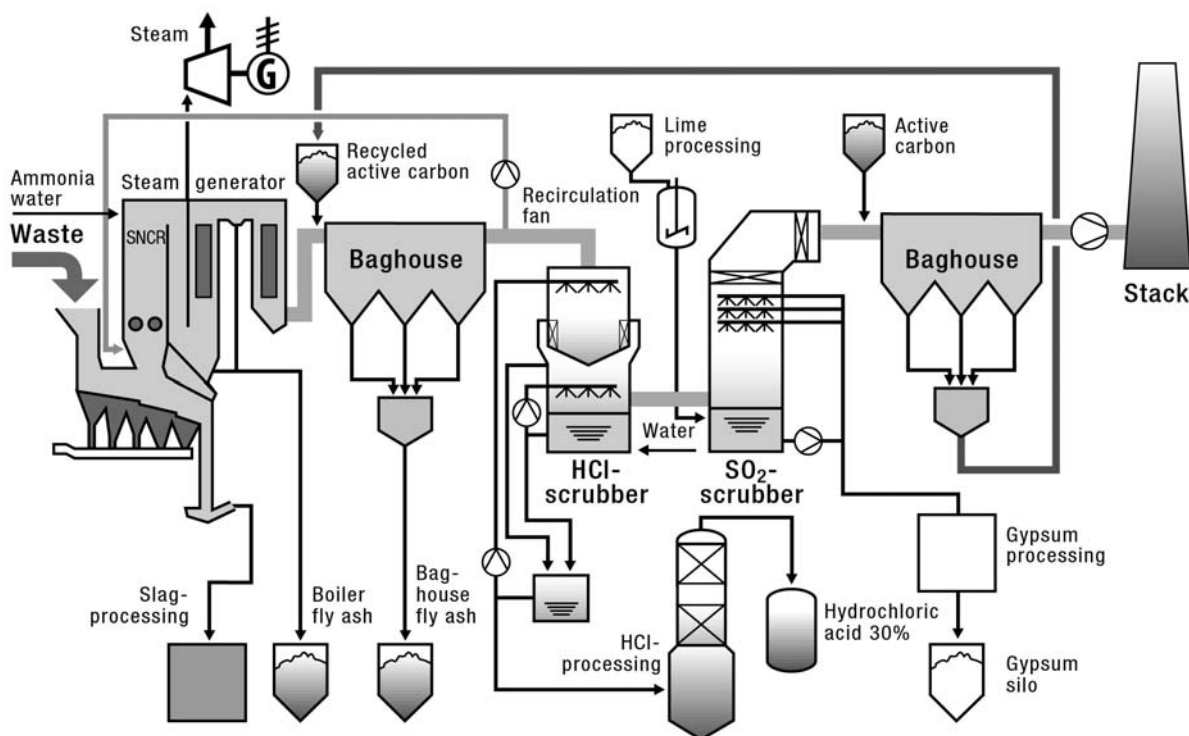


Fig. 1: Flue gas cleaning system at MVR.

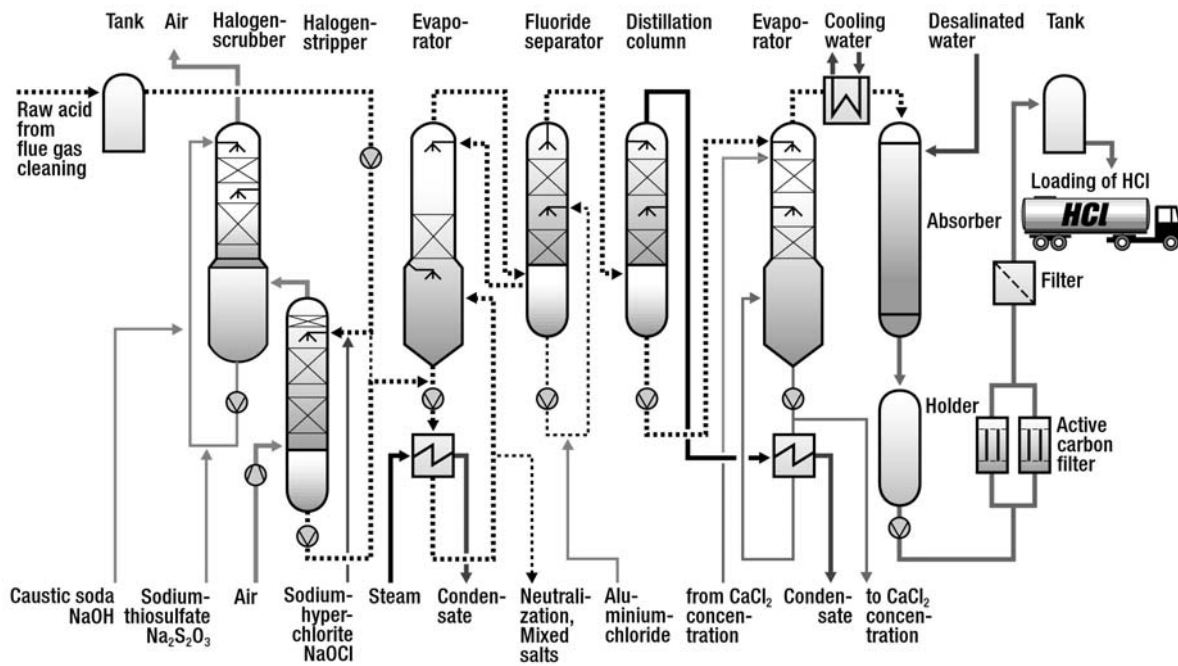


Fig. 2: Process Scheme of MVR HCl Rectification.

extracted as a neutralised solution of mixed salts. They are used as brine for filling salt caverns. Although this method is more expensive than others, it is the most eco-efficient solution for dealing with the chlorine content in municipal waste. This has been verified by an eco-efficiency study.

The PVC waste for the test runs was delivered from March to August 2001, most of it initially for temporary storage on a nearby former power station site. After initial supply problems, the target of approximately 500 t for the test was reached.

The PVC waste was delivered in various shapes and sizes, including dusty waste, large and small rolls, large tarpaulins and sheeting sections, both bundled and unbundled.

In consultation with the waste producers, the PVC waste was classified in accordance with the European waste catalogue as EWC No. 12 01 05. In line with the information from the waste suppliers, approx. 170 kg/h of pure PVC was added to the normal domestic waste in the bunker, as part of approximately 830–1000 kg/h mixed plastic materials. The polymers were mainly thermoplastics (PVC) with a chlorine content of 16%.

The “normal” composition of the waste MVR receives contains about 6% plastic material and 0.7% of PVC waste.

Handling of the PVC waste during the test was sometimes very difficult, the problems arising mainly from long strips (tarpaulin edge trimmings).

Coincineration of PVC took place from August 8th to September 5th 2001; it was only added to Line 1.

Approximately 20 t/d (830–1000 kg/h) was tipped into the waste bunker by a mechanical feeder with a weighing system. Size reduction was partly done in a bulky waste shredder, mainly by hand. The throughput of PVC could be raised to a maximum of 40 t/d, but only for a short period. On average during the test in August/September 2001 the amount of PVC in the waste incinerator was about 5% in relation to an hourly throughput of some 21.5 tonnes of municipal waste.

The crude acid from the flue gas cleaning system was fed from Line 1 to crude acid tank 10 and from Line 2 to crude acid tank 20 to make it possible to process the acid separately in the HCl rectification system.

The average heating value of flexible PVC is around 20,000 kJ/kg, of rigid PVC about 16,000 kJ/kg and of municipal waste about 10,000 kJ/kg. The increased rate of plastic content of the waste with a calorific value of around 18,000 kJ/kg may reduce the incineration capacity of the grate of a waste incineration plant. The steam generators of the MVR plant are designed for a calorific value of 9,750 kJ/kg of the waste at a throughput of 21.5 t/h. The average calorific value in 2001 was around 9,000 kJ/kg. For the quantity used in the test it was not possible to detect any increase in calorific value of the waste as a result of coincineration of PVC waste.

Following the coincineration of PVC waste at the MVR plant in August/September 2001, a short inspection of the steam generator of Line 1 was undertaken. There were no signs of increased corrosion as a result of the increased HCl content. On present knowledge, no adverse influence can

be detected in the MVR plant even with substantial increases in HCl concentrations in the combustion gas. The basic load due to "normal" domestic waste is already very high, with HCl flue gas levels averaging more than 1500 mg/Nm³ at the exit of the steam generator, and concentrations during the test phase were sometimes twice as high.

After the first additions of PVC, a steady increase in density of the scrubbing fluid was observed in the first stage of the HCl scrubber. The output rate was adjusted to take account of the new situation. The average rate was about 1400 kg/h with a mean HCl concentration of 13%. During the test period the scrubbers were sampled more frequently and the contents investigated for relevant parameters.

Most parameters were within the normal fluctuation range of the crude acid without PVC coincineration. Thus, there were no significant differences in the composition of the crude acid between incineration with or without added PVC waste.

Owing to the relatively high HCl levels in the HCl scrubber, initially there was also an increase in the chloride content in the SO₂ scrubber. This also caused an increase in the chloride content in the gypsum suspension tank. There was no increase in the chloride content of the gypsum sold to customers though, because the gypsum is washed and dried in a centrifuge before being stored for shipment.

In 2001 a total of around 3,700 t of 30%-strength hydrochloric acid was obtained from some 306,000 t of waste and returned to the market. At 70%, the recovery rate for chlorine and its compounds is very high. A comparison of the amount of hydrochloric acid produced in relation to the waste incinerated

- normal 12 kg/t waste
("normal domestic waste")
- PVC test 22 kg/t waste
("normal domestic waste" enriched with PVC waste)

demonstrates the successful recycling of the chlorine contained in the waste. PVC waste coincinerated in an appropriately designed waste incineration plant is highly suitable as a "fuel" for the increased production of hydrochloric acid.

To permit optimum crude acid output control from the HCl scrubbers, MVR makes continuous measurements after the steam generator. Normally the mean figure for HCl in the flue gas at the exit of the steam generator is around 1500 mg/Nm³. During the tests that value was twice as high. HCl emission levels in the clean flue gas (stack) nevertheless were very low and were not detectable even by wet chemical analyses.

In the crude gas at the exit of the steam generator for

Line 1 the heavy metal concentrations displayed increased levels of lead. After baghouse 1 or in the clean gas the levels of lead were in the range of all previous measurements.

The PCDD/F measurements during PVC coincineration show no deviations from the usual distribution of the isomers between the lowest and highest values from all previous measurements. Only in the clean gas were slightly elevated concentrations of HpCDF and OCDF detected.

In view of the work of WHO-ECEEH (World Health Organisation – European Centre for Environment and Health) on expanding the list of dioxin-like substances to include twelve polychlorinated biphenyls, PCB's as precursor substances of dioxins and furans were also analysed. The Ballsmiter and WHO PCB values were of the same order of magnitude and are thus independent of PVC coincineration.

The existing measurement data for PAH were supplemented by additional measurements. No dependencies on the input chlorine loads could be detected.

Chlorinated organic compounds, especially polychlorinated dibenzo-p-dioxins and dibenzofurans, play a particularly important role in the public debate about waste incineration. Like the numerous studies to date on experimental plants and other large-scale operational plants with all their plant-specific special features, the assessment of all parameters at the MVR plant during the coincineration tests revealed that PVC has no influence on the quality of the flue gas.

Thus the much-discussed threshold value of 1% chlorine in waste, which allegedly results in increased dioxin formation in waste incineration plants, is not supported by this investigation either.

When processing the crude acid from PVC coincineration, there were no signs of any changes in operation in the HCl-rectification system. The quality of the HCl-acid produced during the test phase does not differ in any way from the acid produced before the test.

By means of normal quality control the other residues – gypsum, slag, baghouse fly ash and boiler fly ash – were also investigated as monthly samples. The results of these analyses show no evidence of any impairment of the substances by the coincineration of PVC waste. The measurements were within the range of the data obtained previously. Under the normal operating conditions of a domestic waste incineration plant in accordance with the 17th Federal Immission Control Ordinance, the higher chlorine content in the incinerated waste does not have any detectable impact on the quality of slag or other residues.

Waste containing PVC is not subject to special monitoring because PVC does not belong to the category of

thermostable halogenated hydrocarbon compounds which display a highly persistent behaviour in the environmental compartments, and can have a toxic effect on the animate world. PVC is not thermostable, and in normal operation of a BAT (Best Available Technology) domestic refuse incineration plant, it undergoes complete combustion at 850°C with the formation of considerable quantities of hydrogen chloride (HCl). The HCl scrubber of the flue gas cleaning system at the MVR plant reliably absorbs up to 3000 mg HCl/Nm³ from the flue gases, without any other negative effects on the flue gas emissions. Given suitable size and shape of the PVC waste and appropriate design of the flue gas cleaning system and the HCl rectification, up to 2% additional PVC waste in the input of the MVR plant in relation to MVR's annual throughput of 320,000 t/a (corresponding to around 6500 t/a PVC) can be handled on a long-term basis without any problems. Mixing with

the normal municipal waste in the bunker and careful mixing of the "waste cocktail" prevents any "thermal" or "chemical" overloading of the system. The frequently discussed opinion that higher PVC levels in the input of waste incineration plants lead to elevated concentrations of heavy metals and/or PCDD/F, PCB in the clean gas and in the products obtained from the flue gas cleaning system was clearly refuted by the test with coincineration of PVC at the MVR plant.

An eco-efficiency analysis has confirmed that waste incineration with separate downstream HCl scrubber and HCl rectification is more expensive than other methods. In the long term, though, it presents the lowest risks because of the high-grade quality of the hydrochloric acid obtained from the combustion and flue gas cleaning, thus offering a cheap and tested alternative to all other methods of PVC recovery under consideration elsewhere.

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