

Treatment of PVC-Containing Nuclear Waste

M. Huntelaar, L. Roobol and V. Smit-Groen

NRG – Irradiation Services, Hot Cell Laboratories, Westerduinweg 3, 1755 LE Petten, The Netherlands

Abstract

The disposal of PVC containing materials in the presence of high active nuclear waste in the past has led to an accelerated degradation of the storage cans on the Petten site containing this type of waste. The origin of this phenomenon lies in the decomposition of PVC under influence of gamma irradiation, in which hydrochloric acid is liberated, which is aggressive to steel.

In the coming years all the high-active waste on the Petten site will have to be transported to the Storage and Treatment Building for High-level Radioactive Waste at the COVRA site in Borssele (The Netherlands). However, to enable this the form of all the nuclear waste has to be chemically neutral. PVC-containing waste, due to the aggressive degradation products, does not belong to this category and will need additional pre-treatment.

A study has been performed on how PVC can be separated from other materials so that the remnants are stable towards high gamma fields. In order to achieve this the following treatments have been studied: dissolving PVC in organic liquids, dissolving PVC in supercritical CO₂, sub-cooling PVC to nitrogen temperatures in order to separate decomposed PVC from the other waste manually, storage of PVC containing waste in resistant containers, and thermal decomposition of PVC.

The outcome of these studies indicates that only a combination of the latter two methods will lead to an acceptable result. In this report a description of all methods will be given leading to that conclusion.

KEYWORDS: high-active solid waste, waste treatment, separation of waste, PVC, poly vinyl chloride

Introduction

In the past, PVC-containing (Poly Vinyl Chloride) items were stored in waste drums together with gamma active materials, or stored in the neighbourhood of gamma active waste. If PVC is exposed to a gamma field for a sufficiently long period of time the PVC starts to degrade, releasing hydrochloric acid. In turn the hydrochloric acid will react with unprotected steel which may cause a threat to the integrity of the waste drums.

During the stock taking of the Waste Storage Facility (WSF) which was performed in the past years, all the waste drums were inspected visually and the dose rate at the surface of each drum was measured. During this inspection it became clear that some of the waste drums had started to corrode. Closer inspection indicated that this corrosion could be correlated with the PVC content.

Corrosion of waste drums

In 1999 a campaign was started to inspect the status of the waste drums in the NRG Waste Storage Facility and to determine the nuclide inventory of the intermediate and high-level active waste. During this campaign, several waste drums were found with corroded surfaces. The origin of this corrosion was unknown, however the status of some of the waste drums made it necessary to immediately repack its content and to investigate the source of this unfortunate occurrence.

During a closer inspection of the waste drums, it was found by X-ray diffraction and by micro-probe analyses that chlorine was abundantly present in the corroded surfaces. Inspection of the

content of these drums showed that PVC-containing materials were the only chlorine sources present. Another observation was that the physical state of the PVC had changed to a more or less tar-like product.

Due to the observed corrosion effect, PVC-containing waste cannot be considered for a straightforward safe storage in waste depositories since only chemically neutral substances are allowed by COVRA. "Chemically neutral" means that the content of the waste is not allowed to change due to chemical reactions. In a separate project, related closely to the development of the NRG Waste Treatment Facility, a study is started to identify potentially suitable methods to neutralise the corrosive behaviour of PVC to the waste drums. Since no solution could be disregarded before hand, the study comprised the following research items:

- Dissolving PVC in organic solutions.
- Dissolving PVC in supercritical carbon dioxide.
- Treatment of PVC at sub-ambient temperatures followed with mechanical waste separation.
- Development of a waste canister able to withstand HCL corrosion.
- Physical degradation of PVC.

This paper contains the results of a more close inspection of these methods research items.

Decomposition of PVC

PVC is known to decompose when exposed to radiation fields such as gamma irradiation, ultraviolet light and heat. Depending on the type of irradiation different decompositions mechanisms exist. However, the first step is always the liberation of hydrochloric acid. In the next steps PVC decomposes further or forms three-dimensional cross-linked structures (polyeens). The latter compounds are very stable and will not release the remaining chlorine as easy as the original PVC does.

Preparation of degraded PVC

Pieces of PVC cloth with similar composition as used in the past and with dimensions of 7 cm x 14 cm were exposed in the Petten High Flux Reactor to a gamma field with dose rates varying from 110 to 240 kGy·hr⁻¹ to an integrated dose of 30 MGy. Chemical analysis showed a reduction in the chlorine content of 32 weight percent for unirradiated PVC to 10 weight percent for the irradiated samples. Unexpectedly, the irradiated pieces of PVC were brittle and blackened in stead of sticky and viscous (figure 1). On the surface of the black PVC remnants, small greasy droplets were observed; the softener. On the aluminium Harwell cans used to contain the samples during the irradiation a white powder was found that could be identified by X-ray diffraction as AlCl₃·6H₂O.

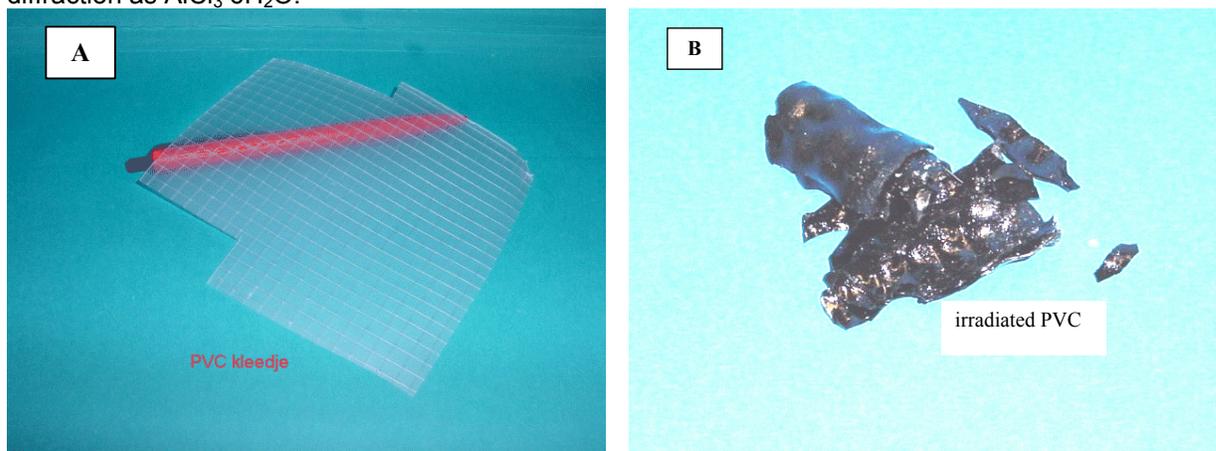


Figure 1 A) the original PVC cloth. B) A piece of PVC after it received a gamma dose of 30 MGy.

Dissolving PVC in organic solvents

Several experiments have been performed to dissolve irradiated (degraded) and non-irradiated PVC samples in organic solvents.

The perfect solvent should pose the following properties with respect to PVC:

- Soluble at room temperature.
- Large capacity.
- Should **not** contain halides.
- Should **not** enhance fire or explosion hazard.
- Solvent should be reusable.

Although some solvents were found in which non-irradiated PVC could be dissolved (dichloro methane, tetra hydro furane and cyclo hexanon), no solvents could be found that dissolved irradiated PVC. Therefore this method was not investigated in more detail.

Dissolving PVC in supercritical carbon dioxide

Introductory experiments were performed which indicated that non-irradiated PVC could be liquefied in super critical carbon dioxide. However, irradiated PVC appeared to be completely inert to this method. A wide range of parameters were tested, such as pressure, temperature, and additives; none of them were successful.⁽²⁾ Therefore this method was not investigated in more detail either.

Treatment of PVC at sub-ambient temperature

The intention of cooling the PVC-containing waste drum to sub-ambient temperatures was to overcome the sticky properties of the PVC waste we found in the waste we repacked in the last year. After the observation that PVC also becomes brittle after irradiation and pulverises under the influence of gamma irradiation, it is expected that unknown quantities of PVC-containing material will be distributed over the waste drums as a powder. Since it is impossible to remove this powder from the waste, no further effort has been made to investigate the route of mechanically removing PVC or PVC-remnants from waste any further.

Repackaging PVC-containing waste in chlorine resistant waste containers

Suitable materials for packaging and storing of PVC-containing drums will have to fulfil the following requirements:

- Resistance against hydrochloric acid (HCl) from the decomposition of PVC.
- Resistance against adsorption agents with basic properties (calciumhydroxide or molecular sieves with a pH varying from 9 to 12).
- Resistance against water, CO₂, CO and organic compounds.
- Long term stability (> 100 years).
- Stable in high radiation fields.
- Shock resistance.

In co-operation with ECN and GNS, a study has been performed to investigate whether there are materials that are able to withstand the aggressive chemical behaviour of the decomposition products of PVC. The most common suitable materials that were identified are ceramics, porcelain and various types of glass. The draw back of these materials is that they are not shock resistant and may not withstand handling at our hot cell facilities and the waste disposal facility or would involve too large investments.

² The super critical experiments were performed in co-operation with the Technical University Delft and FeyeCon, a company specialised in super critical applications.

Another option is to use a lead liner as a first barrier in the waste canister.⁽³⁾ In air, lead will form an oxide (PbO) which is resistant to hydrochloric acid. This imposes that only air can be used as filler gas and no inert gasses like nitrogen or argon, since the oxide layer is only formed and sustained in the presence of a sufficient amount of oxygen. A serious problem (with respect to fire hazards) is the low melting temperature of lead ($T = 327\text{ }^{\circ}\text{C}$).

During the decomposition of PVC not only HCl acid is formed, also other decomposition products such as CO, CO₂, H₂O, H₂ and various organic substances will enter the gaseous phase. If we assume that 10 kg of PVC is present in the waste drums and that a waste canister is able to contain the contents of 27 waste drums, the pressure in the waste canister may reach dangerously high levels ($p > 50\text{ bar}$). This situation can be avoided by adding chemical compounds to the waste that adsorb or react with the gaseous products. Possible additives are CaO(s) and zeolite. A draw back of this approach is that reasonably large amount of chemicals are required, approximately 15 to 20 kg, to stabilise the pressure.

Physical degradation of PVC

As seen above there are several types of radiation that initiate the degradation of PVC: gamma radiation, ultra violet light, and heat radiation. The first one is rather obvious since it is the origin of encountered problems. Employment of this type of radiation to decompose PVC-remnants to an acceptable chlorine concentration is considered. However, knowledge obtained in the preparation of the degraded PVC in the HFR, in which 30 MGy was administered with a moderate dose rate (see **Preparation of degraded PVC**), led only to an decrease by a factor of three in the original chlorine content. This indicates that the use of this route is not very effective. Increasing the dose rate to much higher levels does not automatically means an increase of effectiveness. Besides, the use of a powerful gamma-source to reduce this type of waste is in conflict with the ALARA principle.

Ultraviolet light although much easier to employ is also not considered. The composition of the waste, a mixture of metal scrap, paper, tools, cleaning cloth and so on, is a good shield Ultraviolet light would not be able to penetrate very deep into the waste, making this option very time consuming to use. Decomposition of PVC as a function of temperature has been the subject many studies in the past.⁽⁴⁾ In air PVC is known to decompose under the influence of thermal heat. In inert gasses also degradation will take place albeit reported to occur much slower.

Experiments have been performed to study the release of chlorine from irradiated and non-irradiated PVC. In a series of introductory experiments the behaviour as a function of temperature has been established. Small pieces of material were subjected to various temperature intervals after which they were examined on their residual chlorine content.

It was found that at low temperatures, there was a large release of chlorine, but this did not continue to an acceptable level. Before hand we have set the acceptable chlorine level to 0.001 weight percent relative to the pure PVC. Furthermore, it was observed that large three-dimensional carbon structures were formed. This is in agreement with literature.

³ For the final disposal all the waste currently contained in drums ($\text{Ø } 30\text{ cm} * \text{h } 70\text{ cm}$) will have to be repacked in larger waste canisters ($\text{Ø } 70\text{ cm} * \text{h } 90\text{ cm}$). This canister then would have to be fitted with a lead liner in case the waste contains PVC.

⁴ M.E. Huntelaar, Sanering PVC-houdend Hoogactief Afval: SAPHA, NRG report 20737/02.47546 (Dutch only), May 2002.

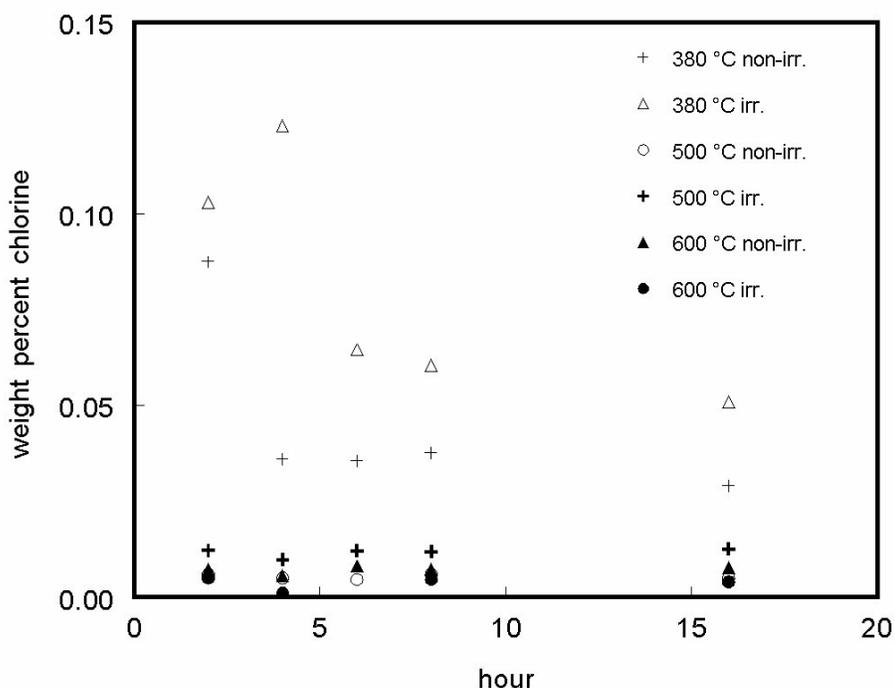


Figure 2 The chlorine concentration of irradiated and non-irradiated PVC samples at three temperatures (380, 500 and 600 °C) as a function of time.

In follow-up experiments the steady state release of chlorine was measured at three temperatures (380, 500 and 600 °C) as a function of time. The results of these experiments show that at 380 °C, significant amounts of chlorine still are present (varying from 0.15 to 0.04 weight percent) and that there is a distinct relation of the concentration with time. At 500 °C and 600 °C, the chlorine content is more or less constant with time and stabilises at approximately 0.005 weight percent (50 ppm), which indicates that the chlorine is liberated in the first hours of the experiment. The graphical results of these experiments are given in figure 2.

Discussion and Conclusion

Poly Vinyl Chloride in radioactive waste decomposes under the influence of gamma irradiation in aggressive hydrochloric acid, which attacks the galvanised waste drums and enhances the corrosion process. Once the waste drums start to corrode, the integrity of these drums is no longer guaranteed, which may lead to a contamination of the waste storage facility.

In a study to investigate how the PVC containing material can be removed from the waste, several options have been investigated:

- Dissolving PVC in organic solutions.
- Dissolving PVC in supercritical carbon dioxide.
- Treatment of PVC at sub-ambient temperatures followed with mechanical waste separation.
- Development of a waste canister able to withstand HCL corrosion.
- Physical degradation of PVC.

It was found that due to the formation of inert compounds (polyeens), all treatments that involve the dissolution of the PVC (and its decomposition products) into a solvent are impossible. Furthermore it is found that sometimes the decomposition of PVC leads to a sticky oil-like substance and sometimes to a brittle compound. The latter effect inhibits removal of the

degraded product from the waste since it will be unfeasible to remove a finely distributed powder from the waste.

A literature study to establish a suitable material, inert to hydrochloric acid that can be used as resistant container showed that lead oxide possesses the best qualities. A complication that has to be dealt with is that due to the decomposition of PVC gaseous products may be formed, such as CO, CO₂, HCl, H₂, H₂O and volatile organic compounds, that may lead to a high-pressure build-up in the final waste canister. This effect can be overcome by adding stabilising agents to the waste that are able to bind the degradation products chemically (solids and gases!). Suitable chemicals are materials are calcium oxide and zeolite.

A draw back of this latter method is that the content of the container is not chemically neutral but that it relies on the neutralising effects of the added chemicals. An effective method to reduce the amount of chlorine in PVC (both irradiated and non-irradiated) is to degrade the material thermally by submitting it to a sufficiently high temperature. Experiments have indicated that at a temperature of 500 °C the chlorine content has dropped to approximately 0.005 weight percent relative to the original PVC mass and that the concentration is independent of time. No further decrease in the chlorine content with increasing temperature could be observed.

By the physical degradation of irradiated and non-irradiated PVC the major draw back of storing the waste directly in a canister can be overcome. The thermal degradation experiments have shown that chlorine concentration in PVC can be lowered with a factor of 6000. Consequently the pressure build-up in the canister due to the formation of degradation products is minimised likewise and its contents are rendered more chemically neutral as without the degradation.

However, since chlorine will still be present in the material, it will be necessary to use a suitable container, resistant to hydrochloric acid. Therefore the conclusion of the study is that the combination of thermal degradation of the PVC-containing waste combined with the use of a resistant container will provide the best option to store the waste. In addition, chemicals can be added to the waste to stabilise the remaining chlorine and to minimise a pressure build-up even further.

In the next step it is necessary to check if it is allowed to use the results obtained from the experiments with PVC in more realistic situations using "simulated" waste. Furthermore, the interaction of the chemicals (used for the stabilisation of the gaseous phase) with lead will have to be checked, and the resistance of oxidised lead against PVC and disintegration products of PVC will have to be demonstrated.

References

1. M.E. Huntelaar *et al.*, Waste Treatment Facility, Proceedings of the International Topical Meeting on Hot Laboratories and Remote handling, XXXIX Plenary Meeting of the European Working Group, Madrid, Spain, October 2002.
2. The super critical experiments were performed in co-operation with the Technical University Delft and FeyeCon, a company specialised in super critical applications.
3. For the final disposal all the waste currently contained in drums (Ø 30 cm * h 70 cm) will have to be repacked in larger waste canisters (Ø 70 cm * h 90 cm). This canister then would have to be fitted with a lead liner in case the waste contains PVC.
4. M.E. Huntelaar, Sanering PVC-houdend Hoogactief Afval: SAPHA, NRG report 20737/02.47546 (Dutch only), May 2002.