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NKS- Project CURES; Combustion of Cables used in Nuclear Power Plants (2024)

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February 2026

Abstract

Project CURES was a project partially funded by NKS in 2024 and a collaboration between Chalmers University of Technology in Sweden and VTT Technical Research Centre of Finland. The project aim was to investigate the combustion of different cables used in nuclear power plants. To do this, the cables a fresh chlorosulfonated polyethylene cable, a chlorosulfonated polyethylene cable that had been subjected to 1 MGy of irradiation, and a Low-Smoke-Zero-Halogen cable were heated up to 200°C, 300°C and 450°C in a tubular furnace and the exhaust gases were sampled with online FTIR to determine their composition and concentration. The same experiment was also repeated with elemental iodine present, and any differences investigated. For the experiments including iodine, a liquid trap was placed at the exhaust to capture any unreacted iodine. These liquid traps were analysed with ICP-MS to determine the iodine content.

The results imply that the two chlorosulfonated polyethylene cables mainly released CS_2/ SO_2, HCl, and a few linear aliphatic hydrocarbons. The irradiated cable consistently gave less releases, but the species were identical. The presence of iodine did not change this behaviour.

The Low-Smoke-Zero-Halogen cable mainly released acetaldehyde. When iodine was added, it also gave ascetic acid and, in the highest temperature, methyl iodide and isopropanol.

Key words

Severe Nuclear Accidents, Iodine, Cables, Combustion

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Final Report from the NKS-R CURES-activity
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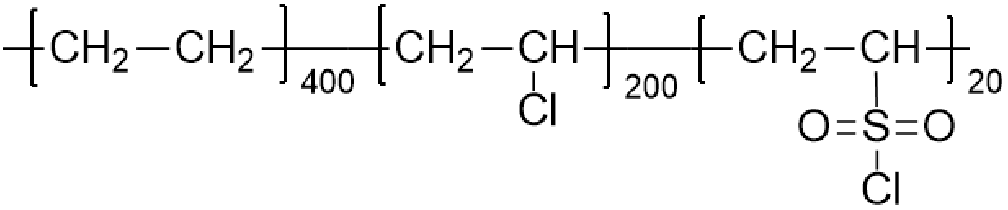
Contents

1. Introduction

The aim of Project CURES was to investigate the combustion releases of cables used in nuclear power plants to gain further insights in what potential organic species can be expected to contribute to the containment and/or sump chemistry. The presence of iodine is also investigated. Iodine is one of the most important fission product, and because its potential to react with organic species and form organic iodides, its presence in this system is worth investigating specifically.

There is not one specific type of cable used for every nuclear power plant. Different plants use different materials depending on when they were built/renovated and who built them. In Sweden, so-called chlorosulfonated polyethylene (CSPE) cables are in use for several nuclear power plants [1]. This type of cable has been investigated thoroughly before, both in terms of mechanical properties [2] and ageing (also when irradiation is considered [3]). However, the combustion behaviour is less studied despite being a potentially important factor for the accident chemistry. Chlorosulfonated polyethylene can be schematically described as in Figure 1 (though the exact ratios of the different polymer groups may vary between different manufacturers).



$$\left[CH_2-CH_2\right]_{400}-\left[CH_2-\underset{Cl}{CH}\right]_{200}-\left[CH_2-\underset{\underset{Cl}{O=S=O}}{CH}\right]_{20}$$

Figure 1: Structure of CSPE rubber.

Most of the cable is normal polyethylene, with some chlorinated polyethylene added, and a few percent of chlorosulfonated polyethylene. This cable confers a good thermal and chemical stability, as well as resistance to ageing.

An alternative type of cable are so-called Low Smoke Zero Halogen (LSZH) cables, used for example in EPR type NPPs. These cables do not have a specific chemical composition, but rather a set of criteria they need to fulfil to be called a LSZH cable. They may not release any halogens when they burn (typically they do not include any halogen at all) and the smoke they produce must be limited. In practice, the requirements are regulated by a pair of standards (IEC/EN 61034-2 [4] and EIC/EN 60754-1/2 [5]). Typically, these cables make use on inorganic fillers, for example $Al(OH)_3$ to inhibit combustion by evolving water upon heating, as described in reaction 1.

$$2\,Al(OH)_3 \xrightarrow{heat} Al_2O_3 + 3\,H_2O \text{ Reaction 1}$$

Iodine is a volatile fission product and pose a significant danger to the public and the environment in case of a severe nuclear accident. Its volatility makes it liable to spread from the reactor coolant system beyond the containment, primarily in the form of CsI [6]; an aerosol, but some portion of the iodine can be expected to occur in the form of a I_2 or volatize from the sump [7] in a later phase. To further complicate the picture, radiolytic reactions between iodine and organic species may occur, resulting in highly volatile species such as methyl iodide (boiling point 42°C) or ethyl iodide (boiling point 72°C). Formation of these substances is also possible in the absence of radiation, but only at high temperatures (400-500°C) [8] which is not expected in the containment at large but may be possible locally.

The CURES project resulted in one scientific publication, which will be published under open access as:" *Combustion of Cables used in Nuclear Power Plants*", which is also available in its entirety as Appendix 1 to this report.

2. Materials, Experiments and Method

Three cables were investigated. A fresh CSPE cable (used as received), a CSPE cable that was subjected to 1 MGy of gamma radiation, and finally a LSZH-cable (used as received).
The temperatures investigated were 200°C, 300°C and 450°C. Each experiment lasted for 30 minutes in the two lowest temperatures, whereas the experiments at 450°C were extended to 1 hour (to ensure the combustion process was complete. Each experiment was performed with and without the presence of iodine. The total 48 experiments conducted are described in Table 1.

Table 1: Experimental matrix.

Cable designation	Temperature [°C]	Iodine presence	Duration [min]	No. of repeats
Fresh CSPE	200	No	30	3
Fresh CSPE	300	No	30	3
Fresh CSPE	450	No	60	2
Irradiated CSPE	200	No	30	3
Irradiated CSPE	300	No	30	3
Irradiated CSPE	450	No	60	2
LSZH	200	No	30	3
LSZH	300	No	30	3
LSZH	450	No	60	2
Fresh CSPE	200	Yes	30	3
Fresh CSPE	300	Yes	30	3
Fresh CSPE	450	Yes	60	2
Irradiated CSPE	200	Yes	30	3
Irradiated CSPE	300	Yes	30	3
Irradiated CSPE	450	Yes	60	2
LSZH	200	Yes	30	3
LSZH	300	Yes	30	3
LSZH	450	Yes	60	2

The experiments took place in a tubular furnace using dry air as the atmosphere. Downstream from the furnace, an online FTIR is placed to sample the exhaust gases. LOD for the FTIR was 2 ppm, and measurement uncertainty is a few percent for the FTIR. However, based on previous experiences, we assume the total combined uncertainty to be 10-20%.

For the experiments with iodine, two further components are needed. Iodine is fed into the system by passing the air over solid iodine crystals held at a temperature of 40°C with the help of a water bath. Furthermore, a liquid trap was placed downstream from the tubular furnace to capture any iodine that penetrated the combustion reactor. The system is schematically represented in Figure 2.

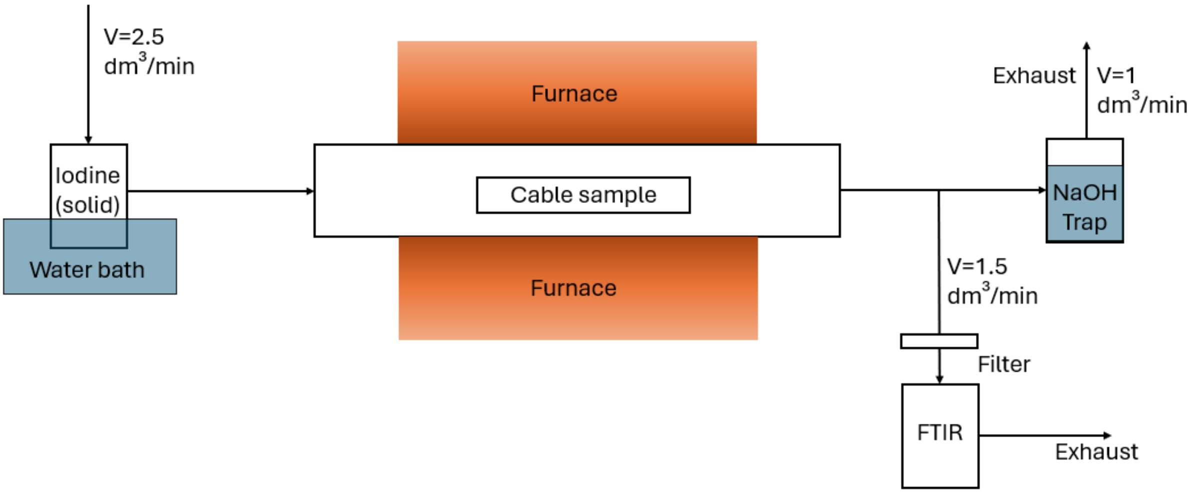


Figure 2: Schematic representation of the system used for the experiments with iodine. For the experiments without iodine, the initial water bath and the liquid trap were disconnected.

3. Key Results

The results of particular interest are the FTIR diagrams for the various processes. Several of these can be found as Figures 3-10 and several other Figures can be found in the attached publication. All three cables have very limited releases at 200°C and the main conclusion to draw from those experiments is that, for the investigated timeframe, the cables appear to remain intact. There is a small release of CS_2 from the fresh CSPE-cable, but that is all.

For the Fresh CSPE cable the main species released at both 300°C and 450°C, no matter the presence or absence of iodine, is HCl. Both CS_2 and SO_2 are also important contributors early in the combustion process. As for the organic species, they are mostly limited to relatively short aliphatic hydrocarbons, though high temperature does give raise to acetaldehyde (C_2H_4O), presumably due to oxidation by the oxygen at these temperatures.

The irradiated CSPE cable behaves almost identically to the fresh one, with the key difference that the magnitude of the releases consistently is lower than for the fresh cable.

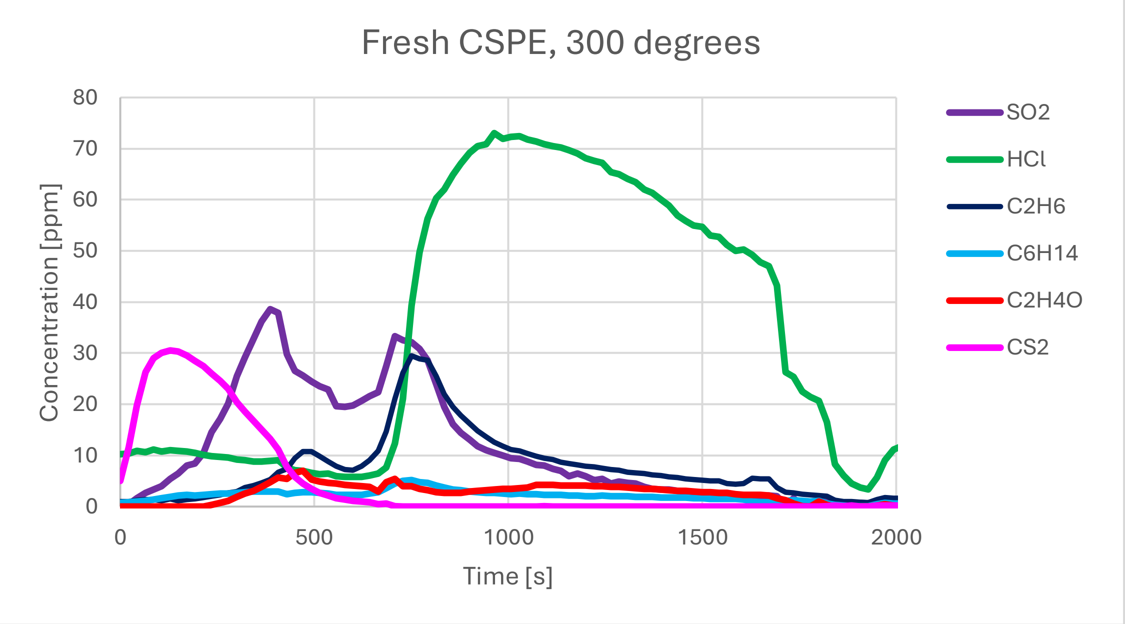


Figure 3: Combustion process of the Fresh CSPE cable at 300ºC

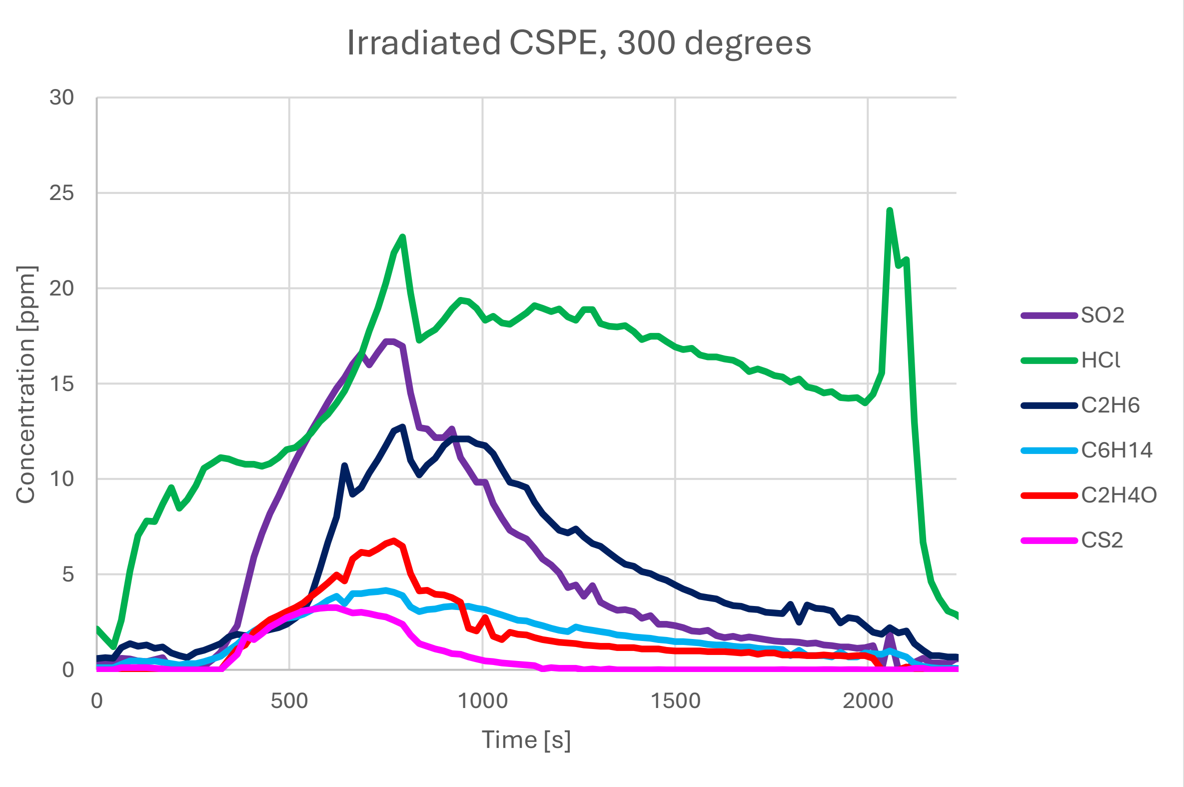


Figure 4: Combustion process of the irradiated CSPE cable at 300ºC. Notice the decrease in concentration compared to Figure 3.

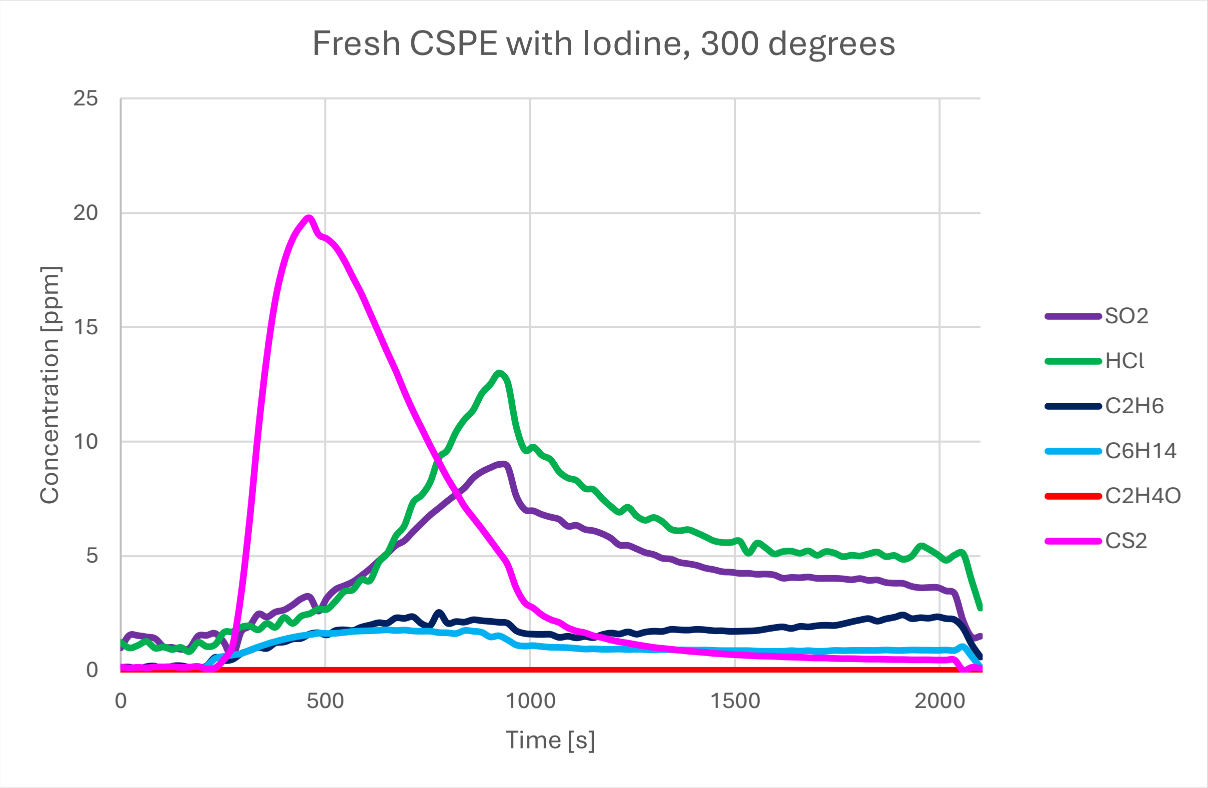


Figure 5: Combustion process of the fresh CSPE cable at 300ºC with iodine present. There is very little change in what species are present.

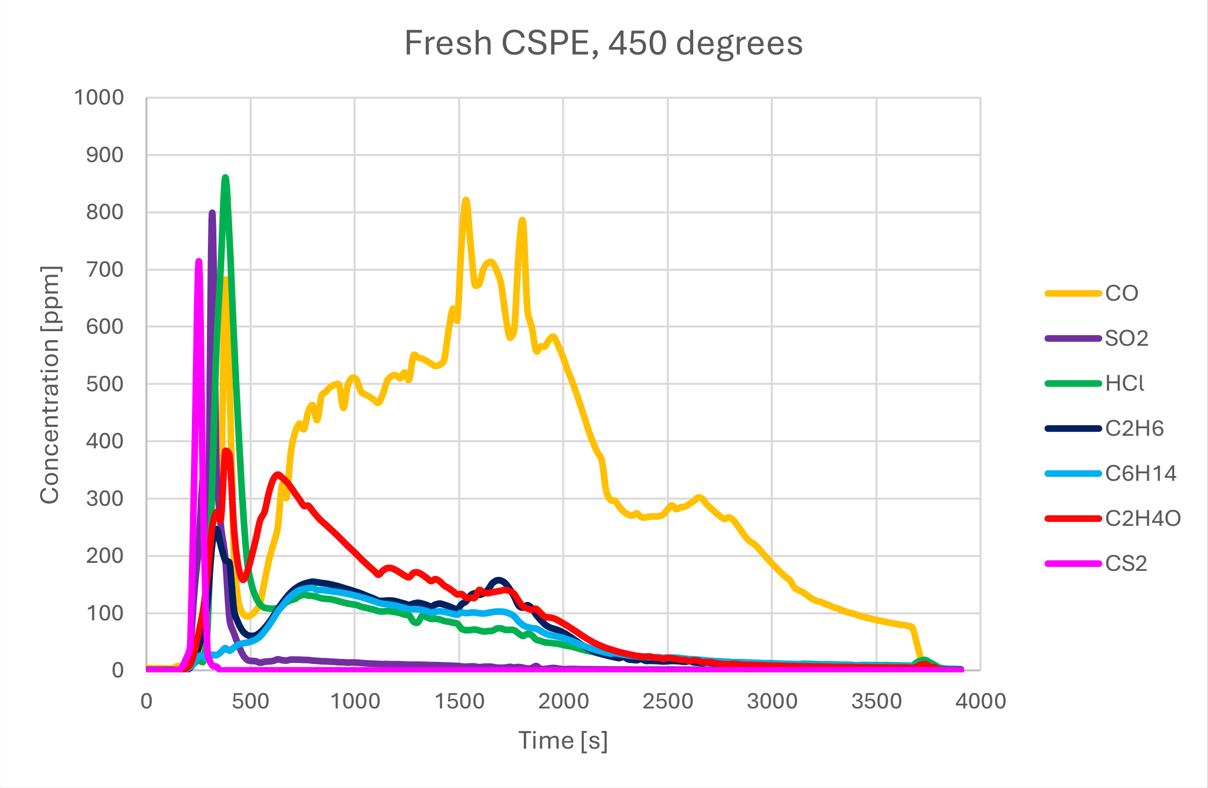


Figure 6: Combustion process of the fresh CSPE cable at 450ºC.

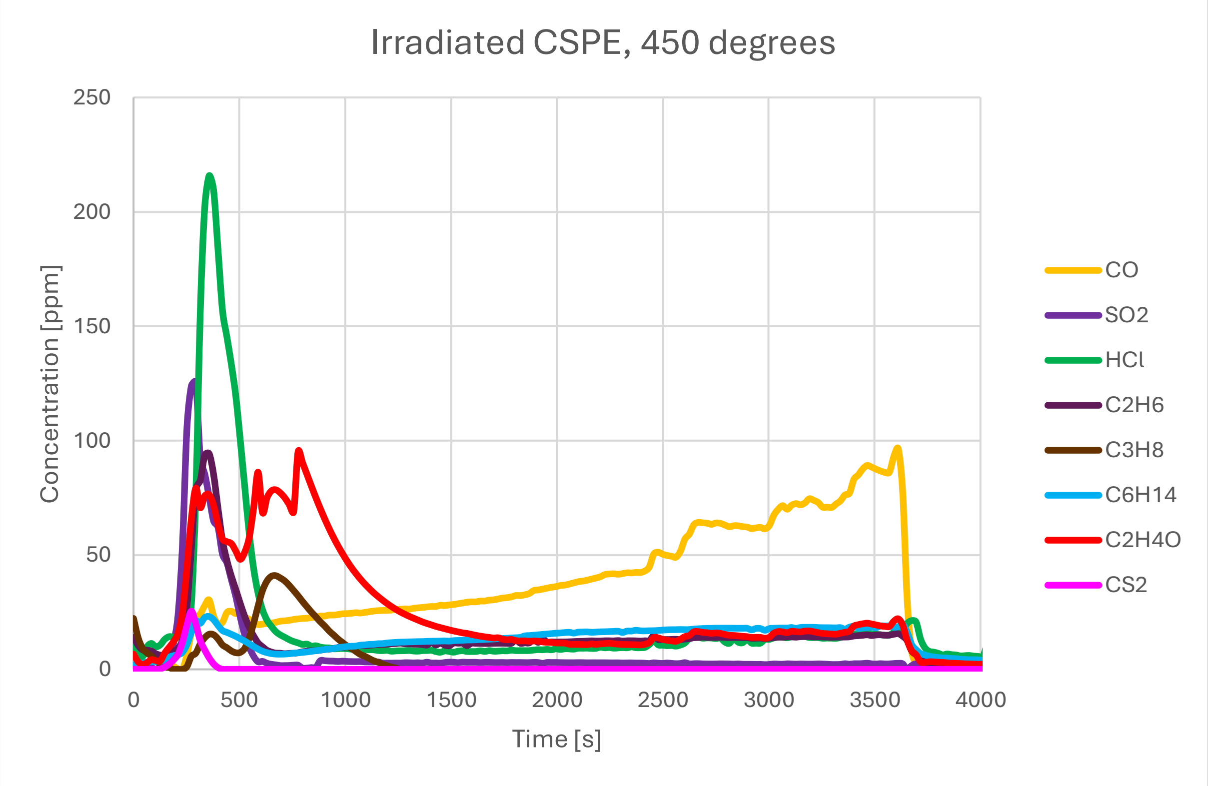


Figure 7: Combustion process of the irradiated CSPE cable at 450ºC. Notice the similarity with the fresh cable without iodine present in Figure 6.

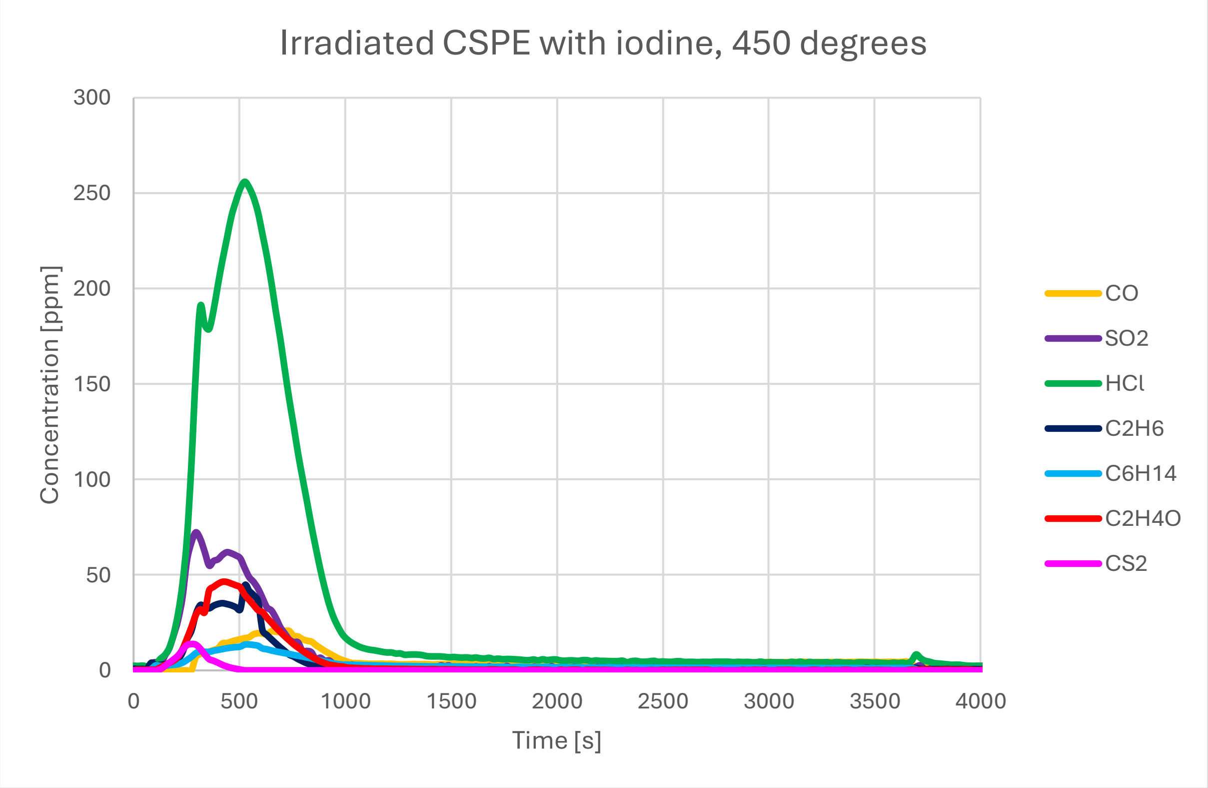


Figure 8: Combustion process of the irradiated CSPE cable at 450ºC with iodine present.

The LSZH cable behaves differently. For both the 200ºC and 300ºC there are barely any releases (the presence of iodine does not change this). For the highest temperature the releases become comparable for most of those of the CSPE cables, though the species changes. As expected, no sulfur or chlorine species can be seen for the LSZH cable. However, the presence of iodine changes the combustion of this cable significantly. Without iodine, the most prevalent species in this case is acetaldehyde (C_2H_4O), with some linear hydrocarbons also being released. Once iodine is present, however, acetaldehyde is only sparingly measured. Instead, the releases are dominated by ascetic acid ($C_2H_4O_2$). There is also a release of isopropanol (C_3H_8O) for about half of the process. In the latter half of the combustion process, isopropanol is replaced by methyl iodide.
This cable releases acetaldehyde when it burns in air. When iodine is added, the acetaldehyde is oxidized further, forming ascetic acid. This acid presumably reacts with any methyl iodide in a methyl addition reaction, which forms isopropanol from the acetic acid. However, towards the end of the experiments when the ascetic acid concentration decreases, the reaction with methyl iodide becomes less likely, and methyl iodide can be measured in the FTIR directly.

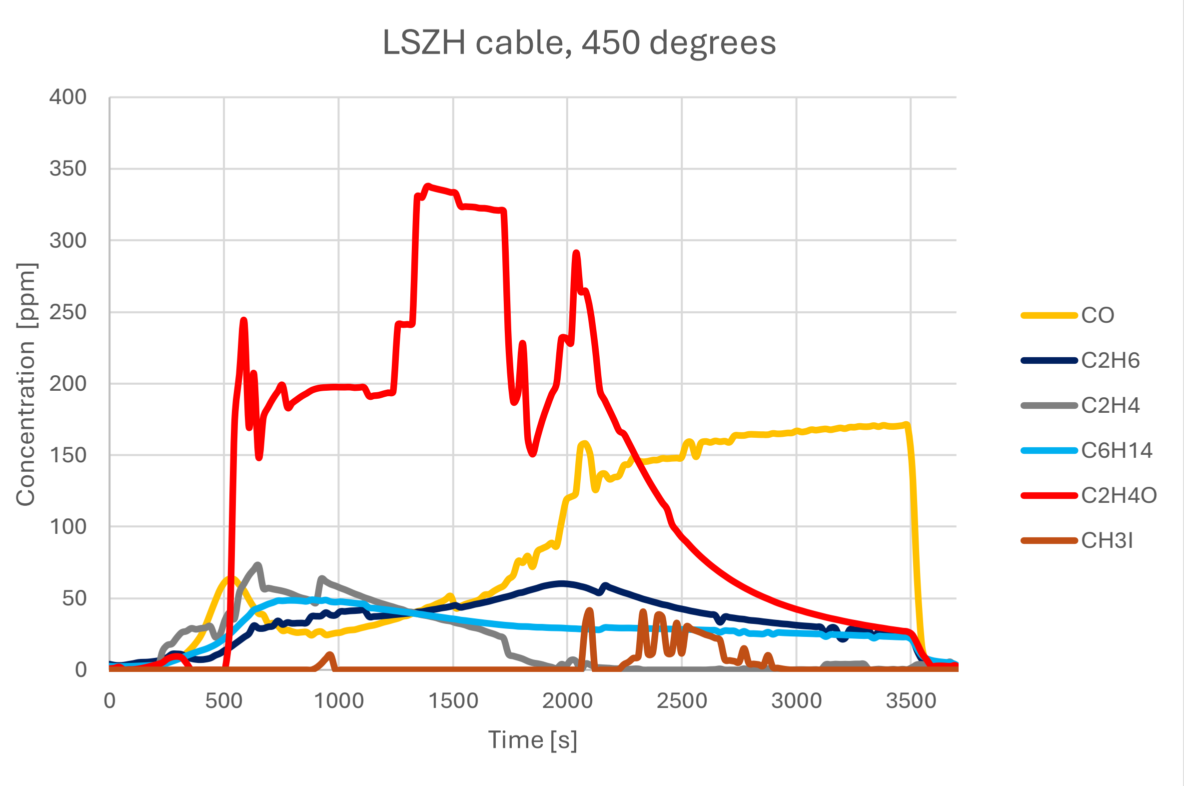


Figure 9: Combustion process of the LSZH cable at 450ºC. The process is dominated by acetaldehyde (C_2H_4O). Note that the CSPE cable only produces acetaldehyde in the presence of iodine, whereas this cable does not need iodine.

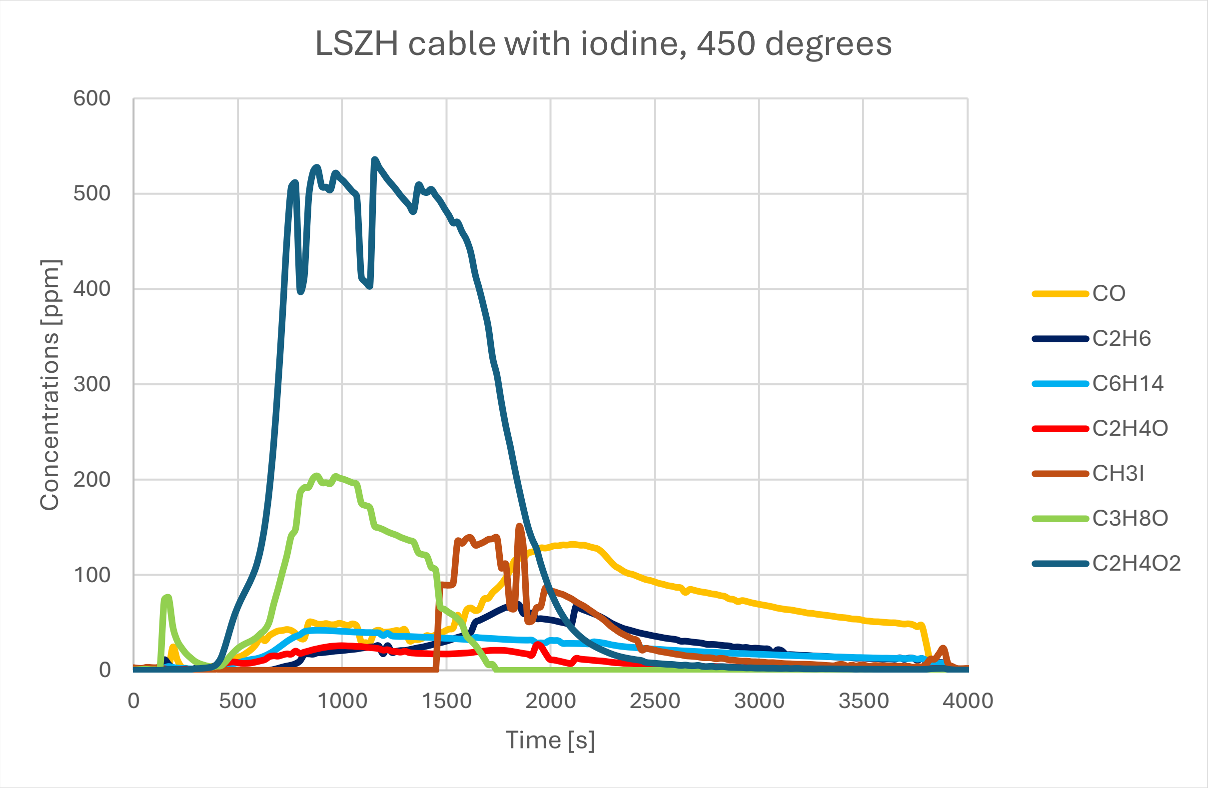


Figure 10: Combustion process of the LSZH cable at 450ºC with iodine present. There is very little acetaldehyde present, and instead the process is dominated by ascetic acid ($C_2H_4O_2$). Notice that methyl iodide (CH_3I) can be detected only after the isopropanol (C_3H_8O) and ascetic acid has begun decreasing.

4. Conclusions

Project CURES aimed to investigate the combustion of cables used in nuclear power plants, with a special interest in weather or not iodine affected the process. The main results are drawn from the on-line FTIR analysis of the combustion processes.

None of the investigated cables produce significant amounts of combustion products at low temperatures in the investigated timescale. Only at 450ºC is there an extensive evolution of volatile combustion products, though there is some combustion of the fresh CSPE cable at 300ºC.

There is a clear difference between the combustion of the cables. The CSPE cable gives raise to several acidic species; HCl and SO_2, especially when the combustion becomes more complete at high temperatures. This potentially has implications for nuclear safety, as acidification of the reactor sump may affect the chemistry, especially iodine. However, how significant this effect turns out to be depends on the amount of cable present, and how complete the combustion is, which in turn depends on the accident. Aside from the acidic species, the CSPE cables tend to give aliphatic hydrocarbons and some acetaldehyde. The presence of iodine made little difference for these cables overall.

The LSZH cable gives almost no releases at temperatures up to 300ºC. At 450ºC it mainly produces acetaldehyde and limited linear hydrocarbons. Methyl iodide was also detected in small amounts. However, when iodine is present, this system changes significantly in that ascetic acid becomes the main species. Methyl iodide is also produced in significant amounts, though it will react with the ascetic acid, if possible, to form isopropanol.

What is clear is that different cables clearly behave in different ways in combustion. This may have implications for the accident chemistry, especially for the potential formation of organic iodides or tellurides. The formation of such species is further made much more likely under radiation [9], which has not been investigated here.

5. Acknowledgements

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6. Disclaimer

7. References

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8. Appendices

Appendix 1: Peer-reviewed paper: *Combustion of Cables used in Nuclear Power Plants*

Bibliographic Data Sheet **NKS- 510**

Title	NKS- Project CURES; Combustion of Cables used in Nuclear Power Plants (2024)
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RESEARCH ARTICLE

OPEN ACCESS

Combustion of cables used in nuclear power plants

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ABSTRACT

The combustion and subsequent reactions of cables found in nuclear power plants are investigated, including chlorosulfonated cables (CSPE cables) and a Low-smoke zero-halogen cables (LSZH cables). In some cases, the cables are irradiated with 1MGy of gamma radiation before combustion. Iodine is added to the gas phase to investigate the potential formation of organic iodides. The combustion process can be followed online with the help of FTIR. The combustion of the CSPE cable mainly releases HCl, SO_2 and CS_2 and aliphatic hydrocarbons. If the cables are pre-irradiated, the species released are largely the same, but the releases are lower. The LSZH cable required higher temperatures to pyrolyze and gave significant releases of acetaldehyde. This cable was not irradiated. The addition of iodine results in the formation of methyl iodide (CH_3I) for the LSZH cable at 450°C. CH_3I also reacts with other organics released in the combustion, forming isopropanol. The same happens for the unirradiated CSPE cable, but to a much lower degree.

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KEYWORDS
Cables; combustion; nuclear power plant; organic iodide

1. Introduction

A severe nuclear accident is characterized by the release, or the potential for release, of radioactive material from the containment. This makes the radio nuclides themselves vital to study and several such studies focusing on different radionuclides are available [1–8]. However, these studies focus mainly on the direct release of the radionuclides from the source term. In a more realistic case, there will also be other chemical compounds that any released radionuclides can react with. These include organics from paints and cables, and other metals or structural materials. The products formed in these interactions can greatly affect the actual release patterns and thus, also, the total release of radionuclides during and after a severe accident.

An important group of components (with potential impact on the evolution of accident the chemistry) is electric cables. Cable jacket materials make up the outer surface of cables exposed to prevailing conditions in NPP and is thus predominantly available for chemical reactions. Cable jacket materials differ between nuclear power plant, depending on the national legislation and year of construction/refurbishment of the power plant in question.

This paper aims to investigate the organic species released by the combustion of cables in the reactor containment. These include chloro-sulfonated polyethylene (CSPE) cables, both fresh cable and cable subjected to irradiation. Similarly, a low-smoke zero-halogen (LSZH) cable are investigated. In this instance, only a fresh cable is investigated. These cable types are representative of, respectively, the Swedish BWR-type nuclear power plants (NPPs) Forsmark and Ringhals [9], and a new, French EPR-type NPP. Special interest falls on any interactions between the released combustion products and iodine.

2. Background

2.1. Iodine chemistry in a severe nuclear accident

During an accident, the engineered safety systems will likely be triggered. These include the containment spray system, used to wash down any aerosols formed from the gas phase and into the water sump at the bottom of the containment. The spray solution is alkaline (pH ca. 9.3 [10]) but also contains boric acid. The alkaline pH retains the fission product iodine dissolved as I^-, with boron added due to its neutron-absorbing properties.

Iodine is one of the most significant fission products from a radio-hazard point of view. In a severe accident, iodine predominantly tends to form cesium iodide, CsI (cesium being another fission product) [11]. CsI exists as an aerosol and is effectively washed down into the sump by the containment spray system [12]. However, in a real accident, there is potential for radiation-induced reactions which may (re)form iodine [13] or

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lead to the formation of organic iodides [14], some of which are volatile.

A few per cent of iodine can also be expected to exist in the gas phase as I_2, rather than CsI. I_2 is not expected to react thermally with O_2 or N_2 [15] (though the presence of radiation may affect this). During an accident however, organic iodides, such as methyl iodide CH_3I, can be formed from the interaction between volatile iodine and the organics released from containment paint due to radiolysis [16]. These species are even more volatile than I_2 and similarly radiotoxic.

The exchange of iodine between the gas and liquid phases may be described as Reaction 1. This is a purely physical phenomena and does not involve any chemical reaction. While iodine gas is slightly soluble in water, its solubility is increased upon the addition of iodides in the aqueous phase, due to the formation of the highly soluble triiodide ion [15]. The rate of reaction 2 (the forward reaction) is very fast, 6.2×10^9 $M^{-1}s^{-1}$ [17], meaning that this reaction can effectively capture any dissolved I_2. Reaction 3 May also contribute to the dissolution of iodine but the extent depends on the pH. The more alkaline the system, the more important Reaction 3 becomes [15].

Reaction 2 requires iodide in the aqueous phase. In an accident this is supplied by, say, washed-down CsI.

$$I_2(g) \rightleftharpoons I_2(aq) \tag{1}$$

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{2}$$

$$I_2(aq) + H_2O(l) \rightleftharpoons OI^-(aq) + I^-(aq) + 2H^+ \tag{3}$$

Direct interaction between volatile organics and iodine in the gas phase of the containment could be theoretically possible due to radiolysis, but the low concentration of both iodine and organics makes it this unlikely [13]. To further limit this possibility, the organic radicals are likely to react with ambient oxygen [14]. Likewise, a thermal reaction between organics and iodine resulting in organic iodides is possible but only at temperatures beyond what may be expected in the containment (400–500°C for the reaction between methane and iodine) [14]. These temperatures may be reached locally, however, in which case the reaction may become significant.

2.2. Chlorosulfonated polyethylene (CSPE)

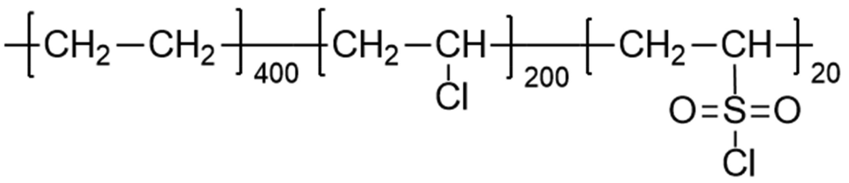
CSPE (also known by the brand name 'Hypalon') cables are used in nuclear power plants due to their good resistance to ageing, chemical degradation and high temperatures (remaining intact up to 130°C, or more for a limited time) [18,19]. The use of this type of cable has been well documented in terms of mechanical properties after ageing [19,20] and irradiation [21,22]. However, combustion of these cables, especially in terms of their chemical releases, is less well-studied.

CSPE is not a homogenous compound but a class of polymers; their exact composition with respect to chlorine and sulfone content will vary depending on the intended use, production method and time of production. Furthermore, factors such as crosslinking, additives, fillers and chain length are all properties that are likely to change which, in turn, changes the material properties. However, all CSPE polymers are formed by polyethylene with a portion of the hydrogen atoms replaced by either chlorine or sulfonyl chloride. Typical contents are about 25–43% chlorine and 0.8–1.5% sulfur (by weight) [23,24]. The chlorination/sulfonation of polyethylene typically results in a random replacement of hydrogen atoms, which also affects the material. The polymer is typically not made up of discrete chlorinated/sulfonated blocks.

CSPE consists of three different monomer types: ethylene, ethyl chloride and ethyl sulfonyl chloride. Depending on the sulfur and chlorine content, the ratio between these will differ for different batches of CSPE. Figure 1 gives a schematic representation of a polymer with typical ratios.

2.3. LSZH cables

LSZH cables are electrical cables designed to emit a limited amount of smoke and halogenated compounds when they burn, typically by making use of hydrated inorganic fillers. These hydrated fillers produce water vapor upon heating, cooling the



$$\left[CH_2-CH_2\right]_{400}\left[CH_2-\underset{Cl}{CH}\right]_{200}\left[CH_2-\underset{\underset{Cl}{O=S=O}}{CH}\right]_{20}$$

Figure 1. Schematic structure of CSPE. Note that the numbers of the different groups are typical values, liable to differ somewhat between samples and manufacturers.

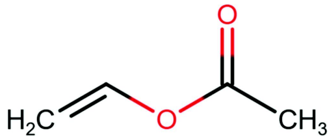


Figure 2. Structure of vinyl acetate. Polyvinyl acetate is very likely used in the LSZH cable.

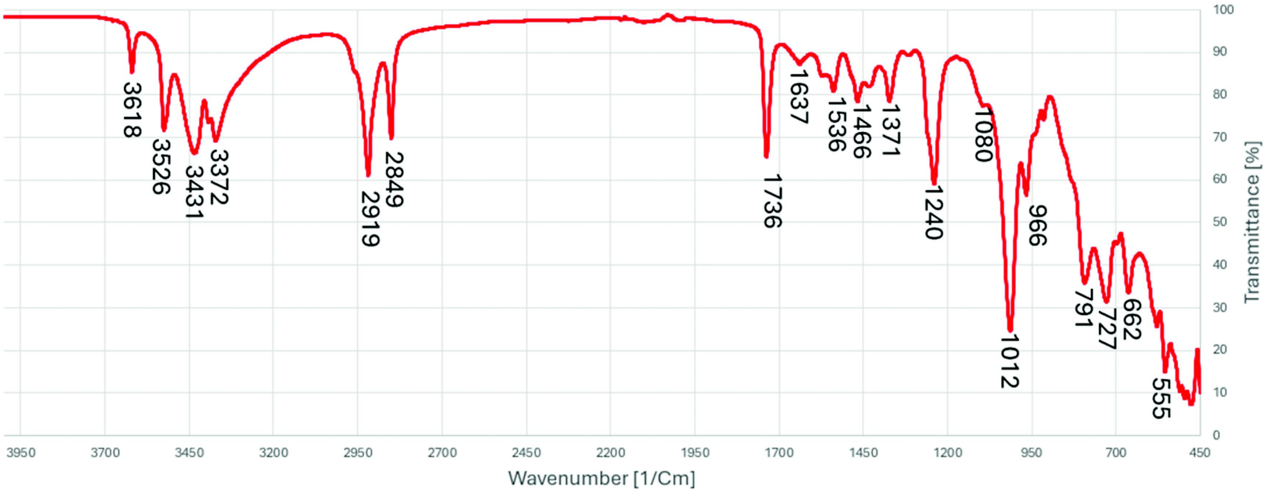


Figure 3. FTIR-ATR spectrum of the LSZH cable. All major layers gave similar results.

combustion reaction and slowing further degradation of the cable. The exclusion of halogens makes for a less toxic fire and simplifies evacuation and firefighting. Chemically, LSZH cables are not one type of material but a classification of cable jacketing materials. Due to its different chemical makeup, an LSZH cable releases different compounds when it burns compared to a CSPE one. The exact chemical makeup used for the cables investigated here has not been conclusively determined, but from the original patent [25] of LSZH cables, (poly)alkenes and (poly) vinyl acetate are mentioned specifically. The structure of vinyl acetate is depicted in Figure 2.

FTIR-ATR was conducted on the LSZH cable, and the resulting spectrum can be seen in Figure 3. The different layers all give very similar spectra. Compared to a reference of a polyethylene-polyvinyl acetate blend, several signals correspond well [26] (most importantly the carbonyl group at 1736 cm^{-1}, and the C-O groups at 1240 and 1012 cm^{-1}), though not all. The outstanding signals are thought to be because the cable likely contains further additives than the pure material (like inorganic filler).

Cable characteristics for both the CSPE cable and the LSZH cable can be found in Table 1.

3. Methods and experiments

3.1. Cable samples

In total, three different cables were used for the basis of the combustion experiments. For the CSPE cables, a freshly purchased connection cable with a single sheet of isolating CSPE rubber around a copper core is used. It was determined that about 60% (by weight) of the cable was jacket material.

The second cable was the same as the first but subjected to 1 MGy gamma irradiation over the course of 15 days. The irradiation took place in a Gammacell 220 (MDS Nordion, Atomic Energy of Canada Ltd.), at a temperature of about 30–35°C and under a continuous (slow) flow of N_2 gas to purge any evolved HCl. The dose rate was about 45 Gy/min. The material, when compared to the fresh, unirradiated cable, appeared relatively unchanged, though it was stiffer. No change in the mass could be detected compared to the unirradiated material.

The third cable was a fresh LSZH cable. This cable was much more complex in its composition, having a total of seven layers, though only three were expected to contribute in a major way to the combustion. From the outside going inwards, there

Table 1. Technical details of the cables investigated.

	CSPE Cable	LSZH cable
Supplier	Belden	Nexans
Maximum voltage [V]	600	600
Maximum operating temperature [°C]	105	60
Conductor material	Tinned copper	Copper
Number of conductors	1	3
Cable diameter [mm]	3.9	11.4

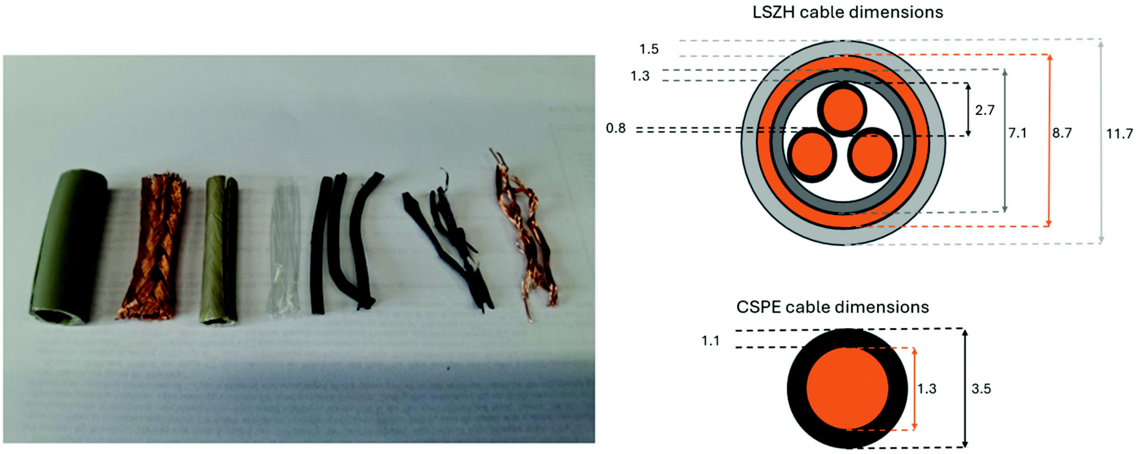


Figure 4. Dimensions of the cable layers for the LSZH and CSPE cables (all numbers in millimeter). To the left a photo of the LSZH cable layers. Note that layers four and six (counted from the right) on the photo are omitted from the figure (they are too thin to measure reliably and have no practical bearing on the dimensions).

is first an outer layer (1.5 mm thick, outer radius 11.7 mm), followed by a copper-wire mesh. The second layer (1.3 mm thick, outer radius, 7.1 mm) covers a bundle of three individual cables (0.8 mm thick, outer radius ca. 2.7 mm), each with a copper conductor core. These three cables are also surrounded by a thin sheet of plastic and the conductor core is bound together by a thin polymeric layer. The layers and schematics of this cable are depicted in Figure 4. In total, 61% of the weight is made up of polymers and 39% is metallic copper.

3.2. *Experiment conditions*

Combustion requires oxygen and so the atmosphere for these tests was synthetic air (21% O_2, 79% N_2, AGA). Three temperatures (200°C, 300°C and 450°C) were investigated to get as complete a picture of the combustion process as possible. These temperatures were chosen to be different enough to capture any significant difference in the combustion processes, whilst being high enough to ensure significant combustion.

In a real nuclear accident, as explained above, steam can be expected to be part of the atmosphere. However, this paper omits steam to focus on the combustion reaction releases themselves and avoid condensation inside the system, as this could interfere with the FTIR measurement by ‘washing’ out any organic compounds. The combustion reaction itself produces some water but not enough to cause any significant issues.

3.3. *Experimental setup and matrix*

The experiments were conducted using a tubular furnace (Entech Vecstar, VCTF 4) with a stainless-steel tube (AiSi 316 L). The cable sample was placed in an Al_2O_3 crucible, and the liquid trap was made of borosilicate glass. Synthetic air (21% O_2, 79% N_2) was fed into the furnace at a rate of 2.5 L/min, controlled by a mass-flow control unit (Brooks S5851, Brooks® Instruments). I_2 is generated from solid iodine crystals placed in a container and volatized by a 65°C water bath. The schematic setup is shown in Figure 5.

The furnace outflow was directed through two different channels. Each experiment involved online measurement using Fourier-transformed infra-red spectrometry (FTIR, Gasmet Technologies Oy) of the exhaust (1.5 L/min). The remaining 1 L/min was directed to exhaust, or, when iodine was connected to the system, through a liquid trap (150 ml 0.1 M NaOH) to capture any unreacted I_2.

In front of the FTIR, there was a filter (47 mm, Millipore, PTFE/Teflon) to prevent particulate matter from contaminating the FTIR. The experimental matrix can be seen in Table 2.

A total of 48 experiments were conducted, investigating the three cables across the three temperatures (200, 300 and 450°C), with and without the presence of iodine. 24 experiments were conducted without iodine to establish a reference for the temperatures. The remaining experiments involved gaseous iodine being fed into the system. Note that for the experiments at 450°C, only duplicates were made, whereas for the rest the experiments were triplicated to ensure calculation of the standard deviation.

The duration of experiments depended on the temperatures. For 200°C and 300°C, each experiment lasted 30 minutes. For 450°C, higher releases were expected, and the duration was increased to 60 minutes.

The experiments were performed by placing the sample in an alumina crucible and pushing the crucible into the furnace hot zone after it had reached the

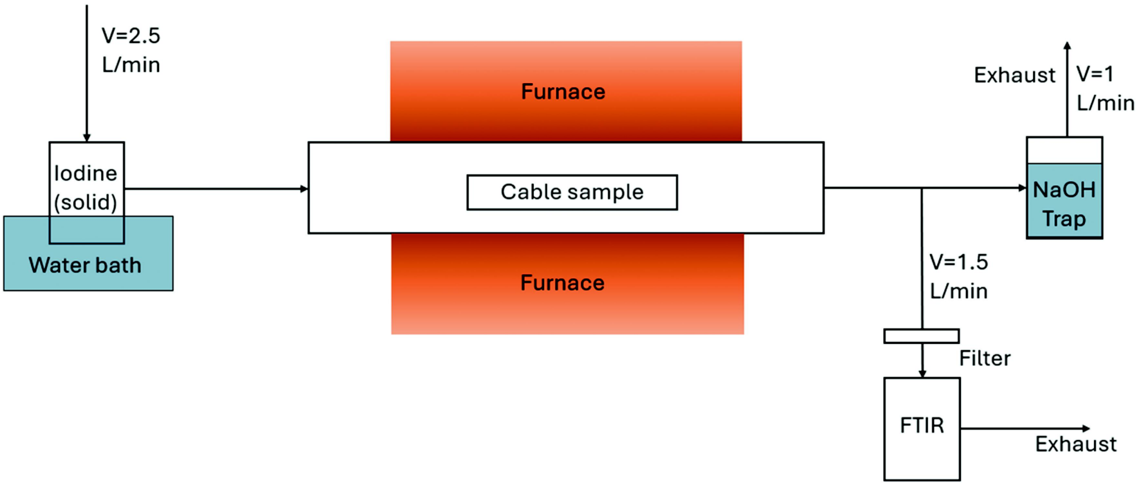


Figure 5. Schematic representation of the system used for the experiments with iodine. The initial water bath and liquid trap were disconnected for the experiments without iodine.

Table 2. Experimental matrix.

Cable designation	Temperature [°C]	Iodine presence	Duration [min]	No. of repeats
Fresh CSPE	200	No	30	3
Fresh CSPE	300	No	30	3
Fresh CSPE	450	No	60	2
Irradiated CSPE	200	No	30	3
Irradiated CSPE	300	No	30	3
Irradiated CSPE	450	No	60	2
LSZH	200	No	30	3
LSZH	300	No	30	3
LSZH	450	No	60	2
Fresh CSPE	200	Yes	30	3
Fresh CSPE	300	Yes	30	3
Fresh CSPE	450	Yes	60	2
Irradiated CSPE	200	Yes	30	3
Irradiated CSPE	300	Yes	30	3
Irradiated CSPE	450	Yes	60	2
LSZH	200	Yes	30	3
LSZH	300	Yes	30	3
LSZH	450	Yes	60	2

targeted temperature (the samples were not subject to the gradual heating of the furnace). The samples were roughly 6 g of cable, in the case of the Fresh CSPE and the LSZH cable and 4 g in the case of the irradiated CSPE. The cables were used as received, with no further preparation.

For the experiments involving iodine, the liquid traps were changed between each experiment. For the experiments at 200°C and 300°C, the same trap was used for the entire 30 minutes. For those at 450°C, the liquid trap was changed every 15 minutes. This was done to avoid saturating the trap, as longer experiments would result in more total iodine being fed in. By changing the trap every fifteen minutes, it was possible to track the change in iodine throughput for these experiments.

Finally, the iodine flow through the system was measured at 300°C, with no cable sample present. This was done to establish a reference iodine mass flow rate. The experiment was conducted by taking samples of the liquid trap after five, 10, 15 and 20 minutes of iodine flow.

4. Results

This chapter presents the important results of the study. However, the majority of the discussion of the results can be found in Chapter 5 (‘Discussion’).

4.1. Filter mass change

The filter in front of the FTIR was weighed before and after each experiment using a bench scale capable of measuring to hundreds of micrograms.

The filter weight measurements (mass accumulation on filter) for the different experiments can be seen in Figure 6.

Figure 6 implies that the presence of iodine affects the combustion, especially at the highest temperature where all experiments in which iodine is present result in a heavier filter. In these experiments, the mass accumulation on the filters at 200°C is low and no conclusions can be drawn, other than that the evolution of soot particles at this temperature is limited. At 300°C, the presence of iodine makes a small difference in filter weight for all samples. The exception was the fresh CSPE cable, where the filter in which iodine was not present was more than three times as heavy as the one with it. At 450°C, the experiments with iodine always gave a heavier filter than the experiments without it. The reasons for this are uncertain but some observations can be made.

Iodine does not interact with the filter material (Teflon) to any significant extent (as evidenced by the fact that no fluorine compounds are ever detected in the FTIR, implying that the filter material remains intact). An alternative explanation is that iodine results in the formation of more/other species compared to the system without iodine. For the LSZH cable, the FTIR supports this.

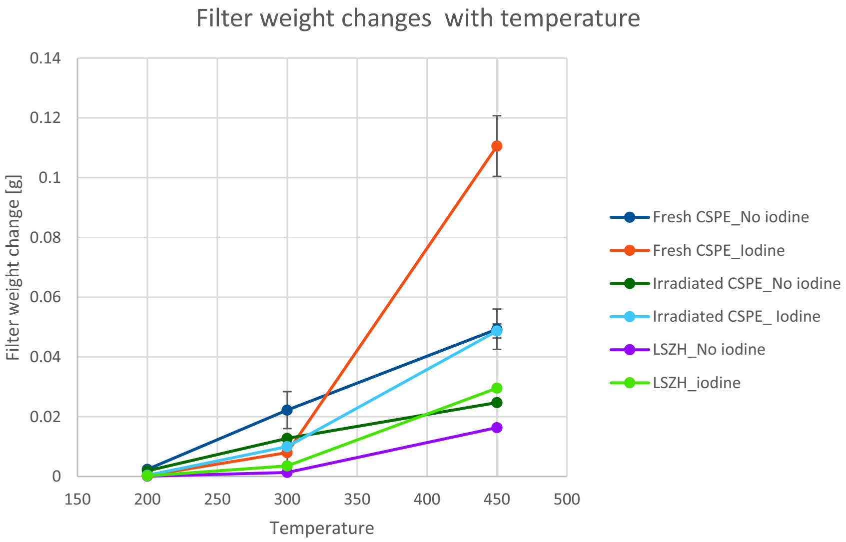


Figure 6. Mass accumulation on filter for the different temperatures and cables in the experiments. Note that, in all cases, the presence of iodine gives a heavier filter at 450°C (but also note that some of the ranges are smaller than the points).

Iodine may also interact with the soot on the filter as the iodine gas passes through it, either reacting or simply being retained in the organic residue from the combustion. Especially in the case of the fresh CSPE, the filter deposit consisted partly of an oily liquid. As I_2 is non-polar, it may be retained in organic liquids. This may partially explain the increase in filter weight.

In terms of mass accumulation on the filters without an iodine feed, the order of releases (in descending order) is fresh CSPE, irradiated CSPE and finally the LSZH cable. This is largely in agreement with the FTIR analysis, in which the LSZH cable tended to measure low concentrations of combustion products. This could be expected, as these cables are explicitly designed to produce little smoke.

4.2. *Liquid trap analysis*

The iodine contents of the liquid traps were analyzed by inductively coupled plasma mass spectrometry (ICP-MS ICAP-Q, Element 2 Thermo Scientific). The samples were diluted 10,000 times in 0.5% ammonia with 1ppb of cobalt ($K_3Co(CN)_6$) as the internal standard. Br^- was also investigated as an internal standard but no significant difference was found between it and $K_3Co(CN)_6$. The system was flushed with ammonia between each sample measurement.

The results of the reference experiments (with no cable present) are shown in Figure 7. Based on the extrapolation, 30 minutes' sampling at 300°C would result in an iodine concentration of about 2.75mmolar.

Table 3 summarises the iodine concentration in the liquid traps after 30 minutes' sampling for the respective low-temperature experiments.

There are major uncertainties in these experiments. Thus, the values cannot be stated as deviating significantly from the reference experiment (± two standard deviations) without cable material present.

Figure 8 shows the time-resolved data for the experiments at 450°C. As only duplicates are available

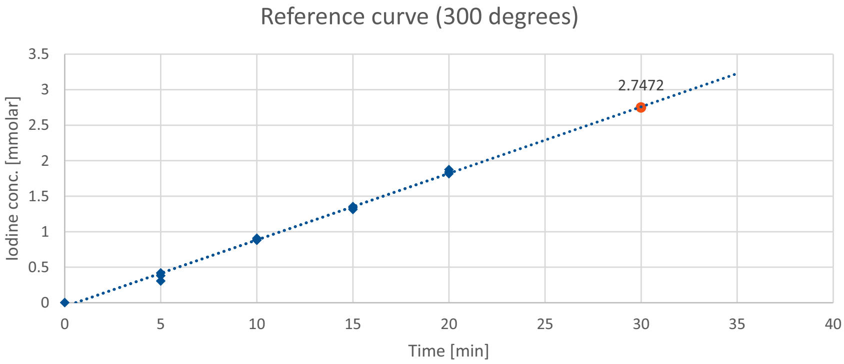


Figure 7. Resulting iodine concentration in the liquid trap after various iodine flushing times. Triplicates are plotted but are very close to each other.

Table 3. Iodine concentration (mean-value and standard deviations) in the liquid traps after 30 minutes' sampling in the experiments performed at 200°C and 300°C in the presence of cable materials. Because the experiments at 450°C are time-resolved and only available in duplicates, they are reported in Table 4.

	Fresh CSPE [mmolar iodine]	Irradiated CSPE [mmolar iodine]	LSZH [mmolar iodine]
200°C	2.2 ± 0.5	3.1 ± 0.9	2.7 ± 0.1
300°C	3.2 ± 0.7	3.9 ± 0.6	3.3 ± 0.4

for these experiments, it is impossible to calculate a standard deviation. However, the results for each pair of experiments often generally agree.

In this case, the liquid traps were changed every 15 minutes (compared to 30 minutes for the low-temperature cases). Thus, the concentration values are lower than in the low-temperature cases. Adding up the iodine fed throughout all the experiments at 450°C gives the total amount of iodine, as shown in Table 4.

At this temperature, both the fresh and irradiated CSPE cables behave similarly. Relatively little iodine is retained in the liquid trap in the first 15 minutes. However, after that, the concentration is steady and comparatively high. The LSZH cable has noticeably less iodine retained in the liquid trap. This might be expected based on the FTIR results, as a noticeable fraction of methyl-iodide forms under these circumstances. It is expected that methyl iodide is less retained by the liquid trap than I_2.

The irradiated CSPE cable consistently shows the most iodine in the liquid trap. This cable is also the one that consistently gives the lowest concentration of organics in the FTIR measurements. This means there are few organics to react with and form any methyl iodide and little organic residue in the system which might retain the iodine there.

4.2.1. A note on the mass-balance of iodine in the liquid trap

The vapor pressure of iodine at 40°C is about 100 Pa [15]. The volumetric flow of air into the system was 2.5 L/min, where 1 L/min was directed through the liquid trap. At ambient pressure (taken to 101,325 Pa), the total number of moles of iodine per minute entering the system can be calculated as in Equation 4 (assuming ideal gases):

$$\frac{n_I}{n_{tot}} = \frac{P_I}{P_{tot}} \rightarrow n_I = 9.6057 \times 10^{-5}\text{moles/ min} \quad (4)$$

where n_I is the number of moles of iodine, n_{tot} is the number of moles in total in the system, P_I is the partial pressure of the iodine and P_{tot} is the total pressure of the system.

In the 15 minutes during which the liquid trap is connected, this gives $1.44\text{x}10^{-3}$ moles in total to the system. If 1 L/min (40%) is directed through the trap and with each trap having a volume of 0.1 L each, that means the maximum concentration of the liquid trap would be 5.76 mM after 15 minutes, or 23.04 after 60 minutes. The numbers measured in the liquid trap are therefore below the theoretical maximum.

The remaining iodine is likely retained in the system pipes. As the temperature decreases from the hot zone in the furnace, some organic residue condenses into an oily liquid and is assumed to retain some iodine. Some iodine may also be able to escape the liquid trap, especially if in the form of organic iodides.

4.3. FTIR analysis

The combustion process was investigated with an online FTIR to determine the combustion products of the different cables at different temperatures and times. As might be expected, the lower temperatures gave very faint results. Only at 300°C and above were

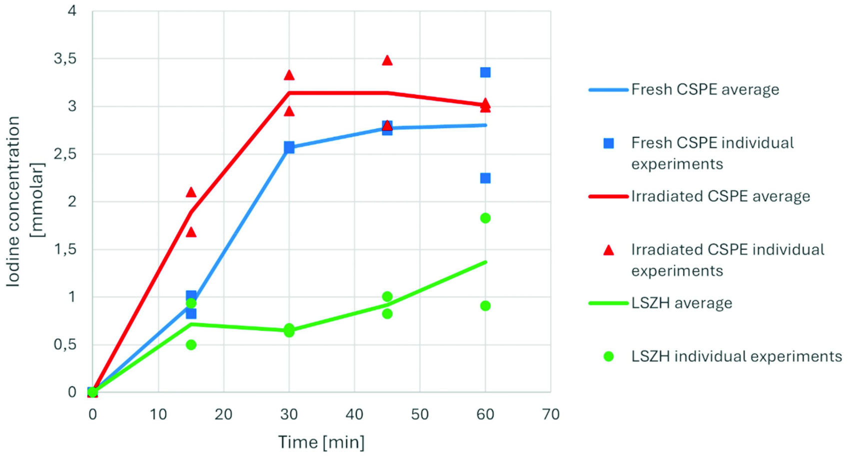


Figure 8. Iodine content of the liquid traps in the experiments taking place at 450°C. Note that the liquid traps were changed every 15 minutes, whereas in the low-temperature experiments this was done every 30 minutes. As such, the results of these experiments should not be directly compared.

Table 4. Iodine concentration (mean value) in the liquid traps after 30- and 60-minutes' sampling in the experiments performed at 450°C in the presence of cable materials.

	Fresh CSPE [mmolar iodine]	Irradiated CSPE [mmolar iodine]	LSZH [mmolar iodine]
30 min	3.5	5.0	1.4
60 min	9.1	11.2	3.7

the concentrations high enough to give meaningful results. Due to the reduced number of experiments at 450°C, no uncertainty estimation is presented for those experiments.

Analysis of the solid residue of the cables, while interesting, falls outside the scope of this paper and will not be further considered.

4.3.1. Low-temperature combustion of the fresh and irradiated CSPE cables

The main species for combustion at 300°C can be seen in Table 5. An example of an FTIR spectrum with the more relevant species can be seen in Figure 9 (fresh CSPE cable) and Figure 10 (irradiated CSPE cable).

As the CSPE cable contains both sulfur and chlorine it is expected that both these elements will be detected during combustion. CS_2 and SO_2 were released early in the combustion of the fresh CSPE cable and the release of CS_2 was followed by SO_2. The literature implies these species are released early/at a low temperature [27] These releases appear to be more-or-less mutually exclusive, as the increase in SO_2 is always accompanied by a decrease in CS_2. SO_2 is present for a large portion of the combustion process. This behavior is related to the exposure of the cable interior, causing a sudden release of stored combustion products.

The most prevalent hydrocarbons are ethane (C_2H_6) and 1,3-butadiene (C_4H_6). As the basic building block of CSPE is polyethylene, ethane can be assumed to form from the breakdown of the polymer. The fact that some heavier hydrocarbons are also detected (such as hexane C_6H_{14}) supports this hypothesis. The formation of butadiene is attributed to the loss of chloride or SO_2Cl groups, giving an unsaturated compound. The general shape of the releases implies a stepwise combustion, in which the outer parts of the cable are burnt first, followed by a decrease in combustion until the cable structure opens up and a 'burst' of combustion material is released.

When investigating the combustion of the irradiated cable, it is apparent that the same species as for the fresh cable appear relevant for this one. The main difference is that the releases are significantly lower for the irradiated cable; typically between one-third and half of the emitted species of the fresh cable. One difference is that C_4H_6 (1,3-butadiene) is not detected in the exhaust of the irradiated cable.

The addition of iodine causes a decrease in releases in both cases which may, at least partially, be explained by the fact that the addition of I_2 (which cannot be seen in the FTIR) dilutes the gas stream and decreases the concentration of all other species. No iodinated hydrocarbons can be measured in either case.

4.3.2. High-temperature combustion of the CSPE cables

At 450°C, many more species are detected and in higher concentrations. An example of the on-line FTIR measurement of the fresh cable is included in Figure 11 (no iodine present). For both repeats of this experiment, the measurements gave similar results in terms of what species were released and at what time. The same experiment with iodine included shows similar results but generally lower concentrations of all species and a slower overall process. An example of such an FTIR measurement can be seen in Figure 12.

The general shape of the releases is not unlike those present at 300°C. CS_2 and SO_2 are still present as a very early release and, again, CS_2 is released first and supplanted by SO_2. However, both are released early and not measured for long. Multiple organic species are also released over a brief timespan and either disappear after that or are released with some continuity. Acetaldehyde is consistently detected and presumably formed from the polyethylene [28].

Moreover, the organics released are similar to the experiments at 300°C, with mostly aliphatic hydrocarbons. The presence of CO is a difference compared to the lower temperature, however.

Upon adding iodine to the system, the general shape of the curve stays the same with a large, early release of HCl, CS_2 and SO_2. The most common

Table 5. Mean concentration of different species released by the fresh and irradiated CSPE cables at 300°C. The values listed are the means of the highest measured concentration in each of the three experiments.

	Combustion products without iodine [ppm]	Combustion products with iodine [ppm]	Combustion products without iodine [ppm]	Combustion products with iodine [ppm]
Species	Fresh CSPE		Irradiated CSPE	
CS_2	30.3 ± 0.3	12.3 ± 4.8	2.3 ± 0.6	<2
SO_2	32.3 ± 5.6	3.8 ± 3.0	13.2 ± 2.6	2.5 ± 0.8
HCl	50.9 ± 23.4	8.1 ± 3.2	21.1 ± 5.1	14.5 ± 1.6
C_6H_{14}	4.3 ± 0.9	<2	4.0 ± 0.6	<2
C_4H_6	45.0 ± 15.5	<2	15.2 ± 2.1	<2
C_2H_6	22.7 ± 7.1	2.3 ± 0.2	11.2 ± 1.6	2.8 ± 0.8
C_2H_4O (acetaldehyde)	5.1 ± 2.1	<2	5.0 ± 1.2	<2

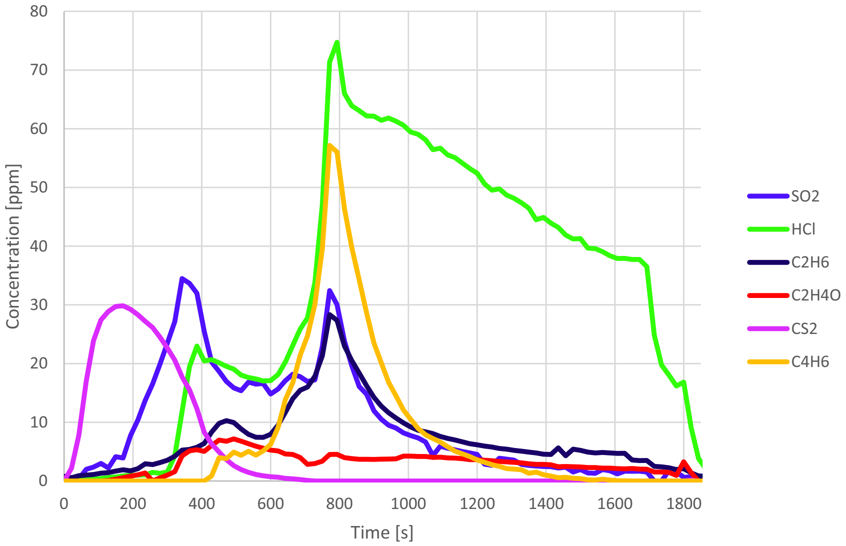


Figure 9. Online FTIR analysis results of a combustion process of the fresh CSPE cable at 300°C. Note that several other species were measured and detected but at very low concentrations. For clarity, only the most prominent species are plotted.

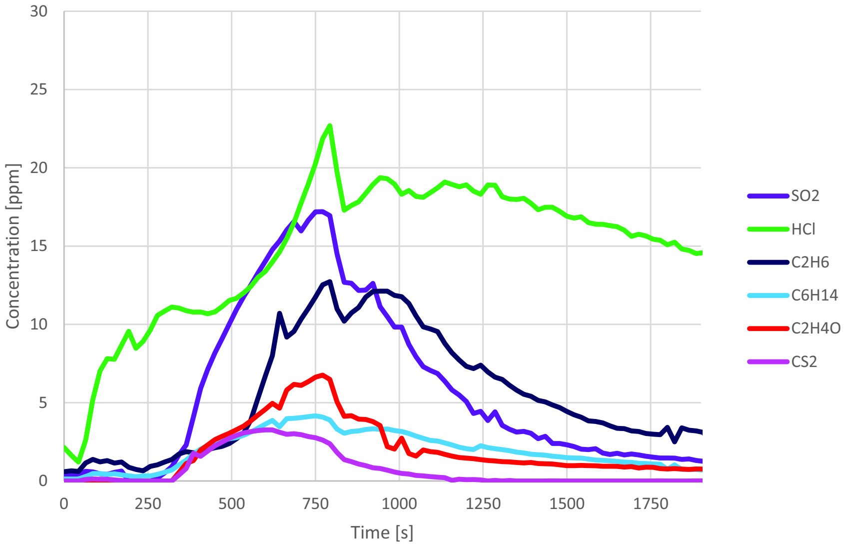


Figure 10. Online FTIR analysis results of a combustion process of the irradiated CSPE cable at 300°C. Note that several other species were measured and detected but at very low concentrations. For clarity, only the most prominent species are plotted.

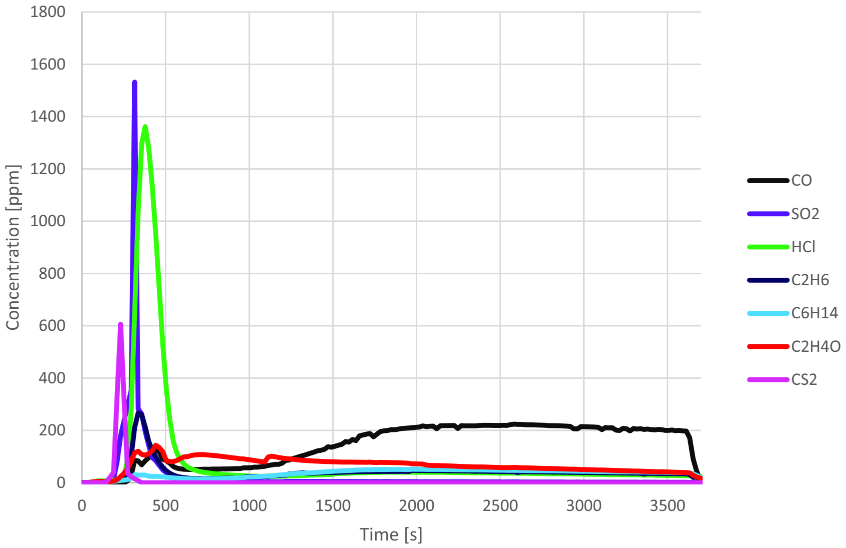


Figure 11. Online FTIR analysis results of the combustion of the fresh CSPE cable at 450°C. There is a significant release of combustion products in the first ca. 10 minutes, followed by a less intense release of, among other species, co.

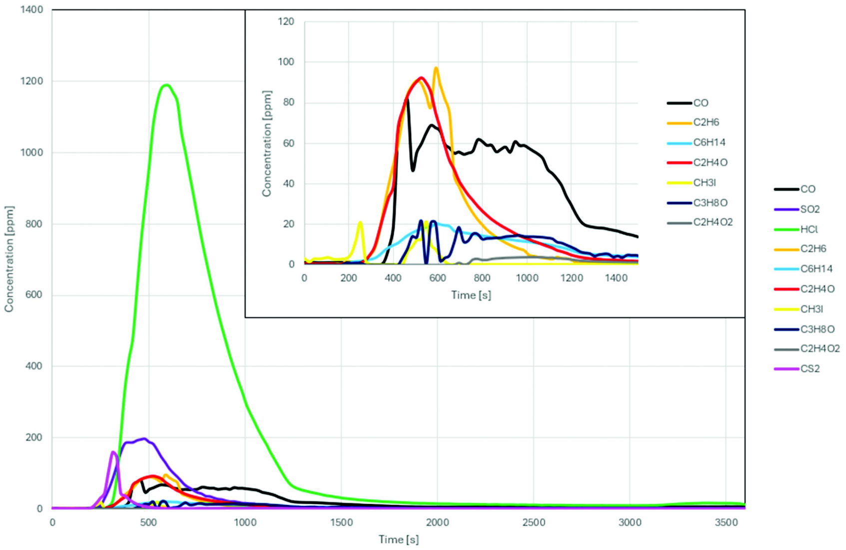


Figure 12. Online FTIR analysis results of a combustion process of the fresh CSPE cable at 450°C with iodine present. Again, there is a rapid release in the early parts of the combustion but, as opposed to the process without iodine, most of the combustion appears complete after about 1500 seconds (25 minutes). A few new species are also detected (see the cut-in image, where HCl, SO_2, and CS_2 have been omitted), including methyl iodide (CH_3I), acetic acid ($C_2H_4O_2$) and isopropanol (C_3H_8O).

hydrocarbon in the 300°C temperature experiment was 1,3-butadiene (C_4H_6). It is completely absent from the experiment at 450°C, presumably due to more efficient breakdown at the higher temperature. Also, interestingly, there are small releases of ascetic acid, isopropanol, and methyl iodide. These species and the reactions forming them will be discussed further in section 5.3.

The irradiated cables behave very similarly to the non-irradiated ones, though the concentrations measured are noticeably lower. In particular, the concentrations of SO_2 and CS_2 have fallen significantly but most hydrocarbons have also decreased compared to the fresh cable.

The time-resolved experiment without iodine, as seen in Figure 13, shows that the general shape of the curve is very similar to that of the fresh cable. Also, just as with the fresh cable, the previously common 1,3-butadiene cannot be measured.

For the case in which iodine is included in the combustion of the irradiated cable, the pattern is practically identical to the fresh one; lower overall concentrations (except for HCl) compared to the same process without iodine. An example of the process can be seen in Figure 14.

4.3.3. Low-temperature combustion of the LSZH cable

For the experiments at 200°C, all the releases were so low that no conclusions could be drawn, except to say that the cable seemed to be almost unaffected by this temperature, at least for the timeframe of these experiments.

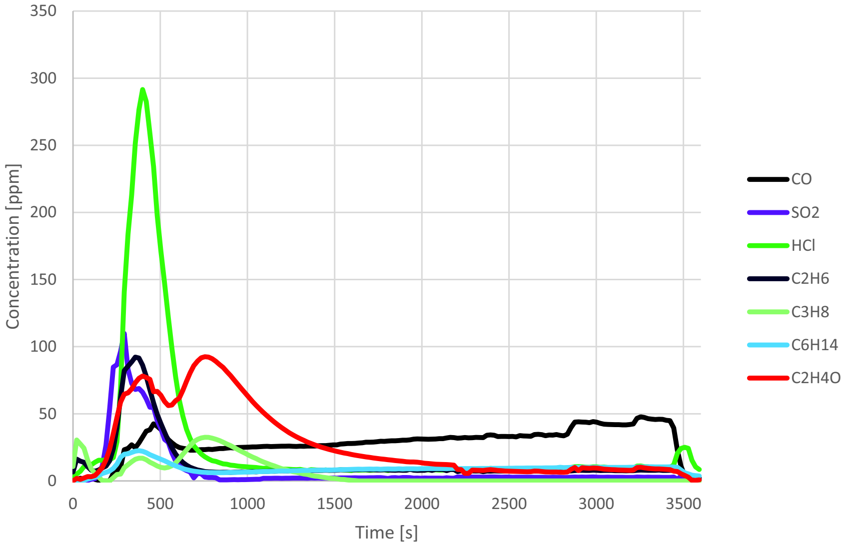


Figure 13. Online FTIR analysis results of a combustion process of the irradiated CSPE cable at 450°C. Note the similarities to Figure 11, aside from the scale on the y-axis.

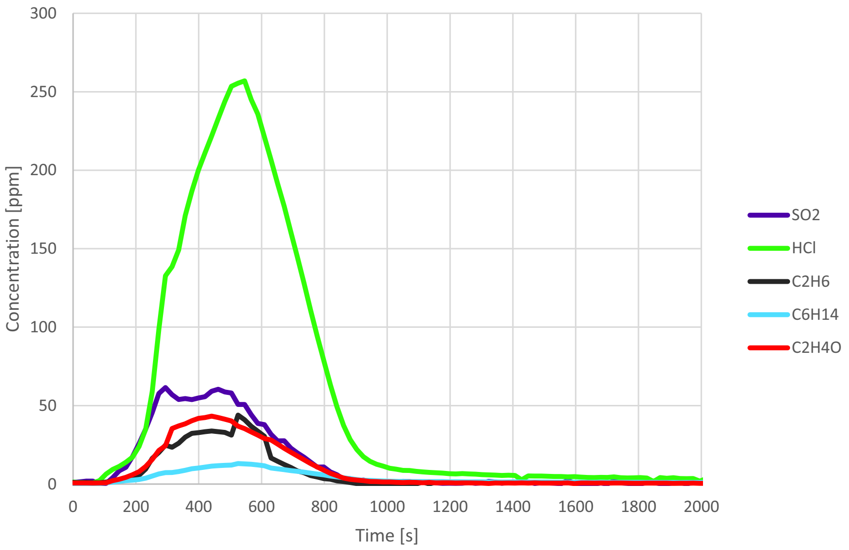


Figure 14. Online FTIR analysis results of a combustion process of the irradiated CSPE cable at 450C with iodine. Note the similarities with Figure 12, aside from the scale on the y-axis.

Table 6. Concentration of different species released by the LSZH cable at 300°C. The values listed are the means of the highest concentration measured for each experiment.

Species	Mean concentration without iodine [ppm]	Mean concentration with iodine [ppm]
CO	4.2 ± 1.5	5.9 ± 1.3
C_2H_4O (acetaldehyde)	5.8 ± 1.5	4.8 ± 0.2
NO_2	2.4 ± 0.2	<2
$C_2H_4O_2$ (acetic acid)	<2	7.9 ± 2.1
C_3H_8	<2	2.8 ± 0.5
CH_3I	<2	2.6 ± ?*

*CH3I was only detected in two of the three experiments (at 4.19 and 3.56ppm).

For the LSZH cable, only a few species appear in significant concentration during the combustion without iodine. They are presented in Table 6. All other species consistently measure below 2ppm. The inclusion of iodine gives rise to several new species being measured in relatively significant concentrations. Most noteworthy is acetic acid ($C_2H_4O_2$), which is the dominant species in this case. Furthermore, the inclusion of iodine did not cause a universal decrease in species compared to the case without it.

4.3.4. High-temperature combustion of the LSZH cable

The combustion profile for the LSZH cable is different from the CSPE cables. Acetaldehyde remains a core species of the process and the aliphatic hydrocarbons make up a small fraction of the combustion products compared to the case of the CSPE cables. One of the concentration measurements of gaseous releases is shown in Figure 15.

The general shape of the releases is different from those of the CSPE cables. The LSZH cable has a longer-running process. Species are measured at

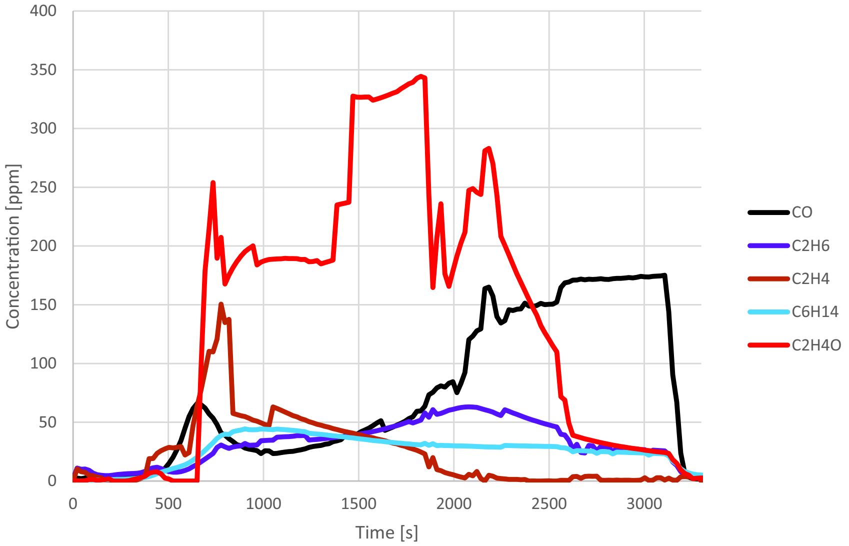


Figure 15. Online concentration analysis of a combustion process of the LSZH cable at 450°C. The process is dominated by acetaldehyde (C_2H_4O) with smaller contributions from aliphatic hydrocarbons.

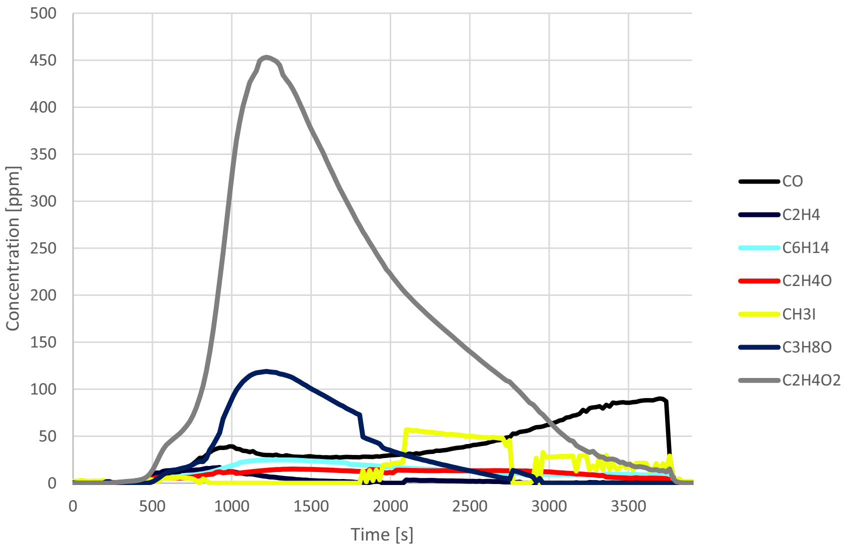


Figure 16. Online concentration analysis of a combustion process of the LSZH cable at 450°C with iodine present. The process is dominated by acetic acid ($C_2H_4O_2$) and isopropanol (C_3H_8O). There is also a clear contribution of CH_3I.

'considerable' concentrations for most of the experiment runtime. Presumably, this is due to the layered structure of the cable requiring more time to break down compared to the CSPE cables. The layered structure is also the presumed explanation for the sudden increase in acetaldehyde at 1400 seconds. Presumably some acetaldehyde is retained in the layered structure, until it breaks down to such a degree that the formed acetaldehyde is released, all at once. This also exposes relatively fresh cable material to the gas stream, which is why the acetaldehyde concentration remains at a higher level before it begins to fall off from 1800 seconds and onwards.

Comparing the process with the results at 300°C, there is a vast difference for the LSZH cable. The experiment at 300°C showed barely any releases, whereas the releases of organic species at 450°C are comparable to those of the CSPE cables.

The process at 450°C including iodine is shown in Figure 16.

The addition of iodine to the LSZH-combustion at 450°C gives rise to several new compounds compared to the process without iodine. Acetic acid ($C_2H_4O_2$) has replaced acetaldehyde as the most important combustion product and both isopropanol and methyl iodide can be detected in considerable amounts.

5. Discussion

5.1. Liquid trap concentrations

The different cables give different amounts of iodine in the trap solutions, as seen in Table 3. For the measurements at 200°C and 300°C, all the measured values are similar and without any obvious pattern. No certain conclusions can be drawn from them. However, as was determined in the reference experiments, any presence of organics appears to increase the amount of iodine caught in the liquid trap, compared to when no organics are present. The reason for this is unclear, but a possibility is that the addition of organic species results in more iodine dissolving because of an increase in ionic strength of the solution. Ionic strength does affect the activity coefficient of all ingoing species of reaction 2 [29]. The CSPE would release HCl and SO_2, increasing the ionic strength significantly, and the LSZH cable could give a similar effect in that it releases acetic acid. This might also explain why more iodine was retained in the liquid traps for the experiments with CSPE cables compared to the LSZH cables.

At 450°C, there is a clear difference between the CSPE cables and the LSZH cable with the latter giving significantly less iodine in the traps. At 450°C, the liquid trap for the LSZH cable captured a similar amount of iodine as at 300°C (the feeding rate of iodine was the same in all experiments) but the high-temperature experiment lasted twice as long as the low- temperature one. Therefore 'Moles of iodine captured per minute' was halved when the temperature was increased. This is assumed to be related to the formation of methyl iodide, which is less soluble in water than triiodide and may therefore escape the trap. These experiments were only conducted in duplicate, meaning no uncertainty analysis is possible.

At 450°C, both CSPE cables gave similar values in the total iodine concentration, about three times the values for the experiment at 300°C. Therefore, even when factoring in the change in experiment duration, more iodine was caught for these cables when the temperature increased.

Looking at Figure 8, for the CSPE cables, the iodine captured in the liquid trap increases to a relatively stable threshold value of ca. 2.7–3.2 mM of iodine after thirty minutes. These first 30 minutes also coincide with the majority of the combustion releases for these cables (as seen in Figures 13 and 14). It appears that the high presence of organics in these experiments decreases the amount of iodine caught in the liquid trap, compared to the experiments at 300°C.

5.2. Considerations regarding combustion of the CSPE cable

The CSPE cables gave mostly similar species as their major combustion products; mainly HCl, SO_2, CS_2, 1–3-butadiene, acetaldehyde, C_2H_6, plus some longer aliphatic hydrocarbons at the higher temperature. The general combustion reaction for a chlorinated hydrocarbon is seen in Reactions 5 and 6 [30]

$$C_xH_yCl_z + \left(x + \frac{y-z}{4}\right) O_2xCO_2 + \frac{y-z}{2} H_2O + zHCl, y \geq z \tag{5}$$

$$C_xH_yCl_z + xO_2xCO_2 + yHCl + (z-y)Cl_2y < z \tag{6}$$

CS_2 is released early and supplanted by SO_2. This behavior is consistent with the overall combustion of CS_2, according to Reaction 7.

$$CS_2 + 3O_2CO_2 + 2SO_2 \tag{7}$$

This reaction was studied extensively before [31] and proceeds through carbonyl sulfide (COS) which is also measured at a low concentration in our experiments. SO_2 is soluble in water and is acidic, further lowering the pH, though it is less acidic than HCl.

HCl will, of course, reduce the pH of the sump which could affect the iodine chemistry. The sump is kept at a pH of around 9.3 to keep iodine in solution in the form of I^-. As the pH decreases, iodine may evaporate as I_2. The extent of the effect of HCl on sump pH depends on the amount of sump solution relative to the evolved HCl, which in turn depends on the amount of cable jacket material and the temperature to which it is exposed.

There were in total eight experiments involving CSPE cables in 450°C. The releases from each experiment can be seen in Table 7. Also included is the total content of chlorine that would be expected in the cable (depending on the weight percentage of chlorine). It is clear that in these conditions, only a small portion of available HCl seems to be released.

Table 7. Releases of HCl at 450°C. Note the difference between the two cables.

Cable type	HCl released [mg]	Amount of cable insulation [g]	Total chlorine content [g]	
			Max [40% Cl]	Min [25% Cl]
Fresh CSPE 1	7	3.6	1.44	0.9
Fresh CSPE 2	8	3.6	1.44	0.9
Fresh CSPE 1 with iodine	15	3.5	1.4	0.88
Fresh CSPE 2 with iodine	14	3.5	1.4	0.88
Irradiated CSPE 1	2	2.4	0.96	0.6
Irradiated CSPE 2	3	2.4	0.96	0.6
Irradiated CSPE 1 with iodine	3	2.4	0.96	0.6
Irradiated CSPE 2 with iodine	3	2.4	0.96	0.6

There is a clear difference between the fresh and irradiated cables, with the latter releasing significantly less HCl, and at 300°C, the fresh cable produces some C_4H_6, which is not seen for the irradiated cable. There are two reasons for this: the radiation induces crosslinking of the polymers [21], making them more thermally resistant, and the radiation serves to release some material from the cable [21]. This is likely the reason for not forming unsaturated species from the irradiated cable. Potentially these species are formed as sulfur and chlorine are released, whereas this has already happened for the irradiated cables and the unsaturated groups have reacted further. The FTIR measurements of the irradiated cable consistently measured very little CS_2, implying its precursor (the chloro-sulfone groups) may be lost due to irradiation. It bears mentioning that no change in the cable mass could be detected as a result of the irradiation.

The presence of iodine also appears to increase the amount of HCl released. This is seen clearly for the four experiments involving fresh CSPE, where the releases of HCl double upon the addition of iodine. In previous studies [32] when CSPE cables were heated to 400°C in a steam-and nitrogen atmosphere with I_2 present, significant portion of the added iodine was bound to the remnants of the CSPE cable. Considering this, and the result seen here, it appears that iodine might be able to replace the chlorine in the CSPE.

If so, this has potential implications for the sump chemistry in two ways. First, the liberation of HCl will acidify the sump, which is a known phenomenon [24,33]. Second, if iodine binds into the CSPE polymer as it degrades, then it may prevent that iodine from being released. However, the extent of this must be studied further. Also, this effect is reportedly less effective when sodium iodide is used as the iodine source. As most of the iodine is expected to be in the form of CsI in an accident, the effect of this interaction has a limit to how much iodine it can be expected to capture.

Many of the hydrocarbons are non-polar and insoluble in water, meaning they can be expected to collect on the surface of the sump. Potentially, this may serve to make free organic species available for reaction with fission products, such as iodine and/or tellurium. However, the feasibility of such reactions will depend both on the concentration of the ingoing species and on the conditions of the accident (including

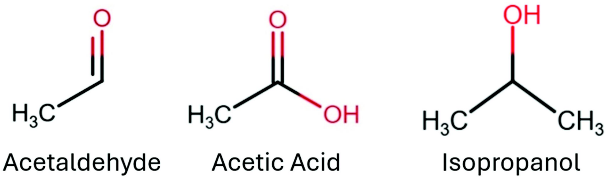


Figure 17. The structure of acetaldehyde, acetic acid and isopropanol.

parameters such as temperature, atmosphere, pH in the sump, radiation field and so on).

In general, the concentration of organic species is lower in the systems including iodine than those without it. This is likely because the added iodine (which is not measurable using FTIR) further dilutes the gas stream, resulting in a lower concentration.

5.3. Considerations regarding combustion of the LSZH cable

The major combustion product for the LSZH cable is acetaldehyde. At lower temperatures, it forms sparingly but at high temperatures it is one of the most-formed organic species. Interactions of acetaldehyde in the sump with dissolved fission products under radiation are unknown but may be worth investigating.

The LSZH cable does not give rise to many combustion products unless the temperature becomes high and, even if it does, it does not give HCl or SO_2. This means that the pH can be expected to be less affected than in the case of CSPE cables. Aside from the pH, the containment chemistry will be affected due to the release of acetaldehyde or acetic acid. Which of these is formed will likely depend on the rest of the containment chemistry, especially the redox conditions.

5.4. Relationship between acetaldehyde, acetic acid and isopropanol

In the experiments with the LSZH cables at 300°C and 450°C, acetaldehyde, acetic acid and isopropanol interplayed with each other. The structures of acetic acid, acetaldehyde and isopropanol are all shown in Figure 17.

Acetic acid can be formed through the oxidation of acetaldehyde, so the loss of acetaldehyde and formation of acetic acid in its place is chemically viable in this system, as I_2 is an oxidizing agent. Given the high temperature, the reaction, as depicted in Figure 18, is expected. Some water evolves in the combustion and is confirmed in the FTIR but is not included in the diagrams. HI would also form from this reaction, but as this species cannot be detected from FTIR it is assumed to decompose back to I_2 and water.

The formation of isopropanol can also be explained through the inclusion of iodine. In Figure 16, methyl iodide appears as the concentration of isopropanol decreases, implying that the isopropanol suppresses the formation of methyl iodide by being formed from a reaction that consumes methyl iodide and acetic acid. Therefore, when the formation of acetic acid decreases (presumably because combustible cable material is starting to run out), this reaction no longer occurs, and methyl iodide can be detected.

From the structures presented in Figure 17, the difference between isopropanol and acetic acid is the replacement of one oxygen with one methyl group. Such a replacement reaction is not the expected reaction with methyl iodide on acetic acid. The typical reaction would be the formation of methyl acetate through methylation. Indeed, a small amount of methyl acetate was confirmed in the FTIR, implying this reaction also occurs. However, the main product was isopropanol.

In Figure 16, the concentration of isopropanol closely follows the concentration of acetic acid, and a decrease in acetic acid is necessary for methyl iodide to be detected. A possibility is that the formation of isopropanol occurs through a radical mechanism enabled by the high temperature, but this explanation is tentative and such a reaction mechanism is unorthodox.

The above process also explains the presence of isopropanol, acetic acid and methyl iodide when the CSPE cables are subjected to iodine (see Figure 12). They presumably undergo the same process, but to a much more limited degree, as the CSPE cables form less acetaldehyde than the LSZH cables.

It is unclear exactly how methyl iodide forms in this system, though it likely involves a radical reaction between iodine (I_2) and any of the organic

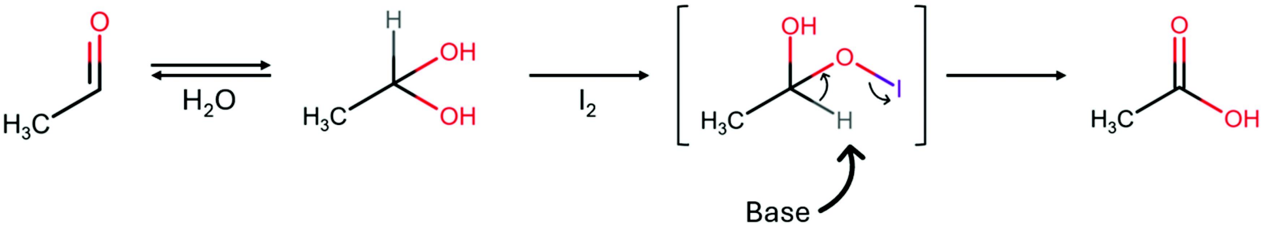


Figure 18. Reaction mechanism for oxidation of acetaldehyde to acetic acid.

radicals formed from the combustion process. Similar reactions are known from the aqueous phase of nuclear accidents [14], and the necessary organic radicals would form as part of the combustion reaction [34].

Isopropanol, if formed according to the above hypothesis, is dependent on the formation of both acetaldehyde and methyl iodide. The latter is especially dependent on the concentrations of the organic precursor and iodine, both of which will likely be low in the case of a nuclear accident. It is therefore not certain that isopropanol will be formed by this reaction, though its presence in, say, paints [35] still make it a species worth considering. If formed, it is miscible in water and will contribute to the sump chemistry.

6. Conclusions

Combustion of the cables used in a NPPs gives rise to multiple volatile species. Depending on the cable type and temperature to which it is exposed, various species evolve, and different consequences may be anticipated.

For chlorosulfonated cables (both irradiated and unirradiated) HCl is a key species. This is important in this context since it can decrease the pH in the containment sump, though the extent depends on how much cable is present and how badly it degrades. The presence of I_2 also appears to affect the releases of HCl quite significantly if the cable is fresh. Other than HCl, the chlorosulfonated cable also evolved aliphatic hydrocarbons, such as C_2H_6, C_4H_6 and C_6H_{14}, with small amounts of C_2H_4O, as well as the sulfur-containing species CS_2 and SO_2. The presence of hydrocarbons would affect the sump chemistry and potentially the containment atmosphere chemistry, as they are volatile.

The irradiated cables in general gave less releases than the fresh ones, especially HCl and sulfur-related species. This is in line with existing literature, as both of these species are known to be affected by radiation and removed from the material, resulting in less chlorine and sulfur available for combustion in these cables [21]. Other releases are either similar or lower for the irradiated cables compared to the fresh ones, likely due to crosslinking of the material making it more resistant to the heat.

LSZH cables do not evolve HCl and give practically no releases at 200°C. The release at higher temperature saw acetaldehyde as the most prominent release from the investigated cable. This species can oxidize into acetic acid in the presence of water, an oxidant (such as I_2), and sufficient temperature. Water will invariably be present if there is an accident, whereas the other factors are less certain but cannot be dismissed.

Experiments confirmed that CH_3I is generated during the combustion of LSZH cables in the presence of gaseous iodine. Although the mechanism for CH_3I generation remains unclear, we also confirmed that the generated CH_3I reacts with acetic acid. It is not thought relevant to the containment at large, though it could potentially occur locally if, say, the corium falls close to the cables. In this study it gave rise to isopropanol, meaning that even though an organic iodide did form, subsequent reactions served to (partially) remove them. Similar reactions were also observed for the CSPE cables, but in a more limited scope.

The question of cable combustion is a complex one, given the large variety of cables available, and accident conditions to consider. Further research is necessary for a continued understanding of this subject. One avenue of interest could be to investigate the leaching behavior of the sump on the cables, especially under irradiation, to determine what organics are then released from the cables. Given the potential acidification of the sump by HCl, changes in pH should also then be considered.

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Data availability statement

Data for this study can be made available upon request.

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