

A New Perspective on Hydrogen Chloride Scavenging at High Temperatures for Reducing the Smoke Acidity of PVC Cables in Fires. I: An Overview of the Theory, Test Methods, and the European Union Regulatory Status

Gianluca Sarti

Reagens S.p.A., Via Codronchi, 4, 40016 San Giorgio di Piano (BO), Italy
Correspondence: gianluca.sarti@fastwebnet.it

Abstract: In the European Union, according to the second basic requirement for construction works of Regulation (EU) n. 305/2011, cables permanently installed in residential and public buildings must be classified in terms of reaction to fire, smoke production, flaming droplets, and acidity. The classification is harmonized; nevertheless, every European Union country decides what kind of classification a cable must have to be installed in a specific location, depending on its fire risk, following the assumption that the higher the fire risk of the area, the higher the fire performance of the cable. According to Regulation (EU) n. 305/2011, the acidity is indirectly assessed by performing EN 60754-2, giving an additional class based on pH and conductivity measurements. Hydrogen chloride (HCl) is one of the gases PVC cables release when they burn. In some applications out of the scope of the Regulation, acid scavengers are commonly used in special-grade PVC compounds to reduce the emission of acidic smoke. In this first part of the paper, the European rules on smoke acidity are presented, a review of the literature on HCl scavenging is performed, and an introduction on HCl scavenging at high temperatures is outlined. The paper shows how different experimental conditions and geometries of the test apparatuses used for assessing the smoke acidity can affect the emission of HCl in the gas phase and what critical issues affect the efficiency of acid scavengers at high temperatures in trapping HCl.

Keywords: acid scavengers; PVC; cables; smoke acidity

1. Introduction

HCl is released when a PVC cable burns, making the smoke acidic. Some fire scientists claim that its diffusion in a fire scenario can incapacitate and hinder a safe escape [1]. Nevertheless, many others highlight that its evaluation is not a critical measure in fire safety and that asphyxiant gases such as carbon monoxide (CO) drive the tenability and, after flashover, CO becomes the dominant intoxicant in fires [2–4]. However, the nature and quantity of toxic substances in smoke modestly depend on the kind of materials in fires. CO is released by all polymers, regardless of their chemical nature (approximately 20% of their weight after flashover) [3,5]. Additionally, CO reaches a high concentration before other intoxicants or irritant substances, such as HCl, can evolve to the gas phase, compromising the tenability conditions [6].

Furthermore, HCl decays quickly in real fire scenarios, and its content is much less than expected from the stoichiometric value in PVC-finished items. HCl is absorbed by “sorptive surfaces,” trapped by fillers in PVC compounds, and washed away by water vapors, and its concentration in the gas phase rapidly goes down [2,3,7].

The heat released by the finished item, particularly the heat release rate, is crucial for assessing whether a small and controllable fire can turn into a large and deadly one, and

therefore if the people can escape unharmed before the flashover is reached [8,9]. Furthermore, the smoke obscuration impedes people from escaping from the fire scenario and being found by rescuers. Therefore, evaluation of the smoke production of the finished items is another strategic parameter, while the assessment of smoke acidity "has no general validity in fire hazard" [3]. Despite these considerations, since 2006 in the European Union (EU), an additional classification for acidity has been introduced in cables permanently installed in buildings, stopping the use of PVC cables in some locations. This paper explains the central principles for creating PVC compounds for cables with extremely low smoke acidity, aiming to get the best classification for acidity. The paper is divided into five parts. Part I is an introduction on the topic of acid scavenging at high temperatures and gives a review of the test methods for assessing smoke acidity, focusing on regulatory status in the EU and particularly on EN 60754-2. It also describes the basic concepts of acid scavenging at high temperatures in the condensed phase and its consequences on flame retardance, smoke production, and acidity.

The following parts show new data clarifying aspects presented in a series of conferences between 2017 and 2022, particularly AMI cables 2019, AMI cables 2020, and AMI formulation 2021: those conferences, regulatory context, and the research on low smoke acidity PVC compounds are described in this letter [10].

The parts are the followings:

- Part II: "Some examples of acid scavengers at high temperatures in the condensed phase";
- Part III: "EN 60754-2 and focus on the species in solution affecting pH and conductivity";
- Part IV: "The impact of acid scavengers on flame retardance and smoke emission";
- Part V: "Comparison between EN 60754-1 and EN 60754-2: what happens to acidity with the introduction of the thermal profile of EN 60754-1 in EN 60754-2".

2. Methods, Regulatory Status in the EU, the Pattern to Low Smoke Acidity PVC Compounds

2.1. List of Abbreviations and Acronyms

- HCl—hydrogen chloride;
- CO—carbon monoxide;
- PVC—poly(vinyl chloride);
- EU—European Union.

2.2. Smoke Acidity Test Methods

Several bench-scale tests can measure the concentration of acidic gases released during material combustion. They can measure the acid content statically or dynamically. The static test methods have a test apparatus based on a combustion chamber, a conveying system, and trapping devices, where the acidic substance is scavenged, analyzed, and quantified (titration, back titration, pH, conductivity, and ion chromatography). The test apparatus of the EN 60754 series and other "old" ones described in the past [11–14] are static methods. Methods with different sample quantities, heating regimes, and test apparatus geometries do not give comparable results.

The dynamic methods follow the concentration of the evolving gas during the combustion of the test specimen. TGA-FTIR, TGA-FTIR-GC-MS, and TGA-MS are the most common ones. FTIR sensors, capable of detecting the released gases and those responsible for making the smoke acidic, can be installed in a cone calorimetry test apparatus. In this way, acidic gases can be viewed "dynamically" during the combustion of the matrix.

The furnace tube is the most common test apparatus for assessing smoke acidity or corrosivity, particularly in some standards, such as the EN 60754 series. The sample, weighted in a combustion boat, is introduced into the quartz tube with a specific heating regime, according to the standard. A normalized air stream collects the fumes in some

bubbling devices, where the ions are analyzed: directly by ion chromatography and titrimetric methods or indirectly by pH and conductivity measures. Methods based on the furnace test apparatus indirectly assess the smoke acidity generated by the burning sample. Measurements in tube furnaces are strongly affected by sample size. If the dimensions of the slices of the test specimen in the combustion boats are too big, char formation can prevent the sample's total combustion, affecting the HCl concentration in the gas phase. The humidity should be carefully checked because moisture in the air flux can bring some chlorides to hydrolysis, freeing the trapped HCl in the gas phase. Even the geometry of the quartz tube and its connectors to the bubbling devices play a significant role. The terminal parts of the quartz tube, external to the furnace, are colder than the inner part. Here, the gas-phase substances can condensate and trap HCl, underestimating its concentration in bubbling devices. The release of trapped HCl can contaminate the successive runs, and therefore terminals should be introduced in the inner part of the furnace to evaporate all condensates before starting a new run.

For the same reason, the tubes, the connectors, the end connectors, and the bubbling devices must be washed carefully, recovering all dissolved HCl. All seals should be well-tightened to prevent the loss of HCl, and tubes must be sized as short as possible to recover all analytes easier during the washing procedures. Without those precautions, furnace tube measurements give poor repeatability and reproducibility.

The temperature and the heating rate strongly affect the emission of HCl of the sample in all kinds of bench-scale tests. If the test is performed at different temperatures and heating regimes, the concentration of HCl in the gas phase will differ [14–20].

2.3. Additional Classification for Acidity in the EU

Regulation (EU) n. 305/2011 (Construction Product Regulation, or CPR) lays down harmonized conditions for marketing construction products in the EU. One of the seven basic requirements of CPR is safety in case of fire; therefore, construction products must meet certain specific requirements in terms of reaction to fire. In the countries of the EU, tests, requirements, classifications, markings, and controls of construction products must be the same. They must have a harmonized classification according to EN 13501-1 and EN 13501-6.

In 2006, the Commission Decision of 27 October 2006, amending the Decision 2000/147/EC and implementing Council Directive 89/106/EEC (CPD), came into effect. It stated that cables permanently installed in the building had to be considered buildings and construction products, and additional classification for acidity had to be assessed. CPR, entered into force in 2017, has implemented the indications of CPD in terms of acidity without any modification in requirements or test methods. EN 13501-6 and EN 50575 lay down the test methods, requirements for getting the reaction to fire classification and the additional classifications for cables, CE marking, and declaration of performance (DoP).

The classes in terms of reaction to fire are the following: Aca, B1ca, B2ca, Cca, Dca, Eca, and Fca (A is more performant than F). The additional classifications for smoke (s1a, s1b, s2, and s3; s3 is less performant), flaming droplets (d0, d1, and d2; d2 is less performant), and acidity (a1, a2, and a3; a3 is less performant) complete the classification of the cable.

EN 13501-6 requires that acidity is indirectly assessed by performing EN 60754-2. The test apparatus of EN 60754-2 is a tube furnace where the sample is introduced and burnt for 30 min in isothermal conditions at temperatures between 935 °C and 965 °C. Two bubbling devices collect the smoke, and pH and conductivity are measured. Table 1 gives the pH and conductivity requirements for getting a specific additional class for acidity according to CPR.

Table 1. Additional classification for acidity and requirements according to EN 13501-6.

Class	Requirement Performing EN 60754-2
Class a ₁	pH > 4.3, Conductivity < 2.5 (μ S/mm)
Class a ₂	pH > 4.3, Conductivity < 10 (μ S/mm)
Class a ₃	not a ₁ or a ₂

If the classification is harmonized at the European level, national codes and regulations of the countries in the EU define the classes the cables should have to be placed in locations depending on their specific fire risk. Thus, cables for medium and high-fire-risk locations must have the best classes regarding reaction to fire, smoke production, flaming droplets, and acidity. Infrastructures, health and care facilities, educational facilities, commercials, industrials, and residential have different fire risks. For example, in Italy, according to CEI UNEL 35016 and CEI 64-8 V4, cables in class B2ca s1a d1 a1 are needed for high-fire-risk locations. High-fire-risk locations are infrastructures such as air terminals, railway stations, marine stations, subways, road tunnels longer than 500 m, and railway tunnels over 1000 m long. In medium-fire-risk locations, such as health and care facilities such as hospitals, nursing homes, assisted residences, entertainment, educational facilities such as cinemas, theatres, discos, schools, museums, and residential with more than 24 m height, cables Cca s1b d1 a1 are needed. Other locations, such as residential and commercial buildings less than 24 m in height (houses, bars, restaurants, shops, and medical offices) need bunched cables in class Cca s3 d1 a3 and single wires in class Eca. PVC compounds are suitable for manufacturing cables to match the class B2ca s1 d0 a3 [19,20], but nowadays there is no PVC compound for cables in class a1 or a2. Therefore, PVC cables are excluded in medium- and high-fire-risk locations. According to CPR, cables are the only buildings and construction products with an additional classification for acidity. The same is not required for other finished items such as flooring, linear insulation for pipes, and all finished items ruled by EN 13501-1.

In the EU, the market share of PVC compounds for wires and cables was 65% in 2000, which will be 35% in 2023, as forecasted in [21]. CPR has driven the growth of halogen-free cables [21], but other standard products, excluding a priori PVC compounds, do the same. The research in developing PVC compounds with a low smoke acidity lies in this regulatory context.

2.4. Definition of Acid Scavengers at High Temperatures

An acid scavenger is a “tool” for trapping acid substances through a reaction or a physical absorption, and it can even be designed to trap specific acidic substances. Acid scavengers discussed in this paper are specific to HCl. Acid scavengers acting as co-stabilizers for processing PVC compounds can be organic and inorganic substances. However, for working at high temperatures, the acid scavenger must be inorganic and stable during and after the combustion of the finished item. HCl scavengers have two main action mechanisms: scavenging in the gas phase and scavenging in the condensed phase.

An alkaline gas, neutralizing HCl, can reduce the smoke acidity in the gas phase, yielding products able to be transported by convection in the gas-phase stream. If EN 60754-2 is performed, these products can reach bubbling devices and dissolve electrolytes. In this kind of acid scavenging, the conductivity is therefore severely affected by the dissolved electrolytes. An example of this scavenging is when some precursors of NH₃ (such as melamine, urea derivatives, and ammonium octamolybdate) are used as flame retardants. In halogen-free systems, the TPU typically gives this kind of behavior, a high pH but extremely high conductivities, when EN 60754-2 is carried out due to specific flame retardants and charring agents releasing ammonia. For example, some TPU jackets for charging cables for electric vehicles must be flame retarded according to EN 50620 and IEC 62893 and cannot reach conductivities less than 10 μ S/mm.

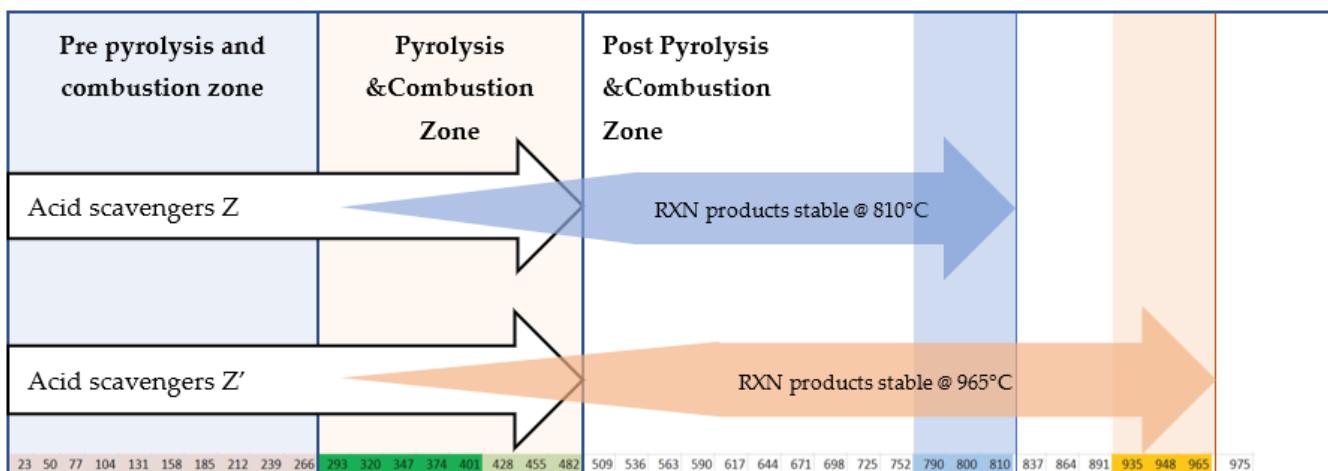
The action mechanism in the condensed phase is triggered by a solid acid scavenger trapping the gaseous HCl in a solid or liquid reaction product. This scavenging minimizes the contribution of other electrolytes in bubbling devices, except for non-scavenged HCl. Therefore, HCl is the driving force behind pH and conductivity.

This paper discusses scavenging in the condensed phase.

2.5. Acid Scavenger at High Temperatures in the Condensed Phase: Failures and Success

2.5.1. Where, When, and How

When a PVC compound is subjected to heat flux, the temperature increases, and three main zones can be identified: (a) pre-pyrolysis and combustion zone; (b) pyrolysis and combustion zone; and (c) post-pyrolysis and combustion zone. Scheme 1 visually represents the three main zones.



Scheme 1. Identification of the three main zones. The blue zone is the temperature range of EN 60754-1, and the orange one of EN 60754-2. Temperature in °C, “@” means “at.”

The pre-pyrolysis and combustion zone is where thermal fluxes are low, and stabilizers play their fundamental role in preventing thermal degradation through HCl's well-known “zip elimination” [22]. In Scheme 1, the ranges of this zone are determined by all ingredients affecting the thermal stability of the compound, thus mainly stabilizers, but also the PVC resins, flame retardant fillers, plasticizers, and fillers. As the temperature increases over 270–300 °C, stabilizers end their action, the PVC compound starts the pyrolysis, and the evolving gases start their combustion. The PVC compound contains organic and inorganic additives. When the compound pyrolyzes, it makes free flammable and inflammable volatiles. Flammable volatiles burn, and the fire is supported by species such as H and OH, bringing energy to the flame. HCl is the primary, inflammable substance in the gas phase and plays a strategic role in trapping those radicals [23]. This phenomenon is common for all halogenated polymers and is called “flame poisoning.” It is the reason for the inherent flame retardancy of PVC.

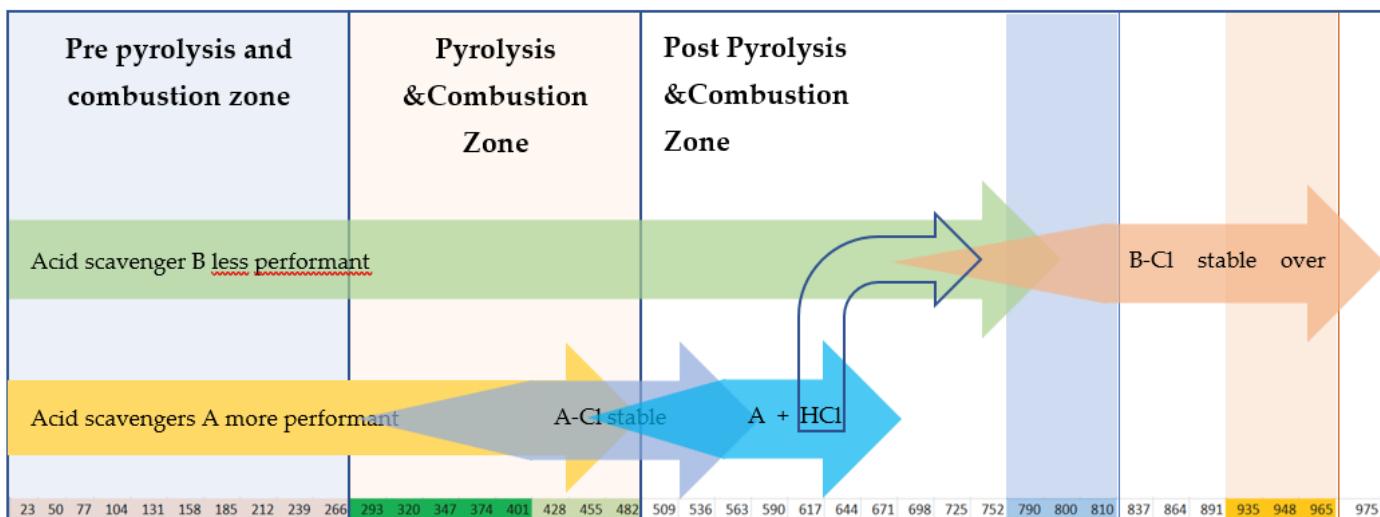
Wu and others have described the pyrolysis mechanism of PVC resin by a two-stage pyrolysis model [24]. However, the pyrolysis and combustion of PVC compounds for cables are made more complex by the presence of some additives. The kind and quantity of the volatiles released in the gas phase depend on the ingredients in the compound. The volatiles in the first stage of the degradation are mainly plasticizers, HCl, CO₂, CO, and benzene, while aliphatic hydrocarbons, CO₂, and CO are released in the second stage. If there is CaCO₃, another step centered at 750–850 °C is visible, related to its decarbonation. When all the organic substances are entirely burnt, the post-pyrolysis zone starts, where the stability of the reaction products coming from the reaction of the acid scavengers with HCl is crucial for getting low values of smoke acidity. Therefore, a substantial reduction

of smoke acidity depends on the effectiveness of acid scavengers in holding and trapping HCl in solid ashes without any decomposition up to the maximum temperature required by the acidity test method. Performing EN 60754-1, the reaction product must be stable up to 810 °C and up to 965 °C if EN 60754-2 is carried out (Scheme 1).

2.5.2. Single-Step Reaction Versus Multiple-Step Reaction

References [16,17] claimed that acid scavengers could react through single- and multiple-step reactions. In their opinion, a single-step reaction involves just one acid scavenger following Scheme 1.

References [16,17] also claimed that, in PVC compounds, depending on the kind of ingredients, it is possible to also have multiple-step reactions involving more than a single teammate, following the “relay race scheme” in Scheme 2. Here the performant acid scavenger A can react with HCl, creating A-Cl. If A-Cl is unstable, the second less-performant acid scavenger B gets HCl from A-Cl decomposition. If this HCl release is slower than that coming from PVC, and if B-Cl is stable, this “relay race scheme” brings a synergistic effect and increases the scavenging efficiency. Acid scavenger B can be added to the dry blend, or a precursor of B can yield B during the combustion. Multiple-step reactions can use more than two teammates. Part II of this paper will enter more into the details of multiple-step reactions, providing some examples.



Scheme 2. Multiple-step reactions in HCl scavenging at high temperature. Temperature in °C, “@” means “at.”

2.5.3. Main Failure Cases

Following the schemes mentioned above, the failure cases generating high smoke acidity should be mainly two: the kinetics of the scavenging action by an acid scavenger and the decomposition of the acid scavenger or its reaction products. If an acid scavenger has a slow kinetic in its reaction with HCl and the kinetic of the evolution of HCl is too fast, most of the HCl quickly reaches bubbling devices.

The Kinetics

Kinetics are strictly linked to the following:

- The chemical nature of the acid scavenger;
- Its particle size;
- Its dispersion properties;
- The test temperature and heating regimes.

1. Chemical nature

The higher reactivity of the acid scavenger, the quicker its reaction with HCl. So strong bases, such as hydroxides or oxides, are more efficient than weak scavengers, such as carbonates.

2. Particle size

The smaller the particle size, the more efficient the reaction is. Therefore, ground calcium carbonates (GCCs) are less efficient than ultrafine precipitated calcium carbonates (PCCs).

3. Dispersion

The better the acid scavenger dispersion, the more intimate contact with PVC, and the quicker the reaction with HCl. Furthermore, the zones in which acid scavenger misses emit massive amounts of HCl. It is worthy of mention that a finer particle size additive can bring about a worse dispersion of an acid scavenger in the matrix.

4. Temperature and heating regimes

The higher the temperature, the quicker the evolution of HCl from the burning matrix, and the more complex the chance for a solid acid scavenger to trap gaseous HCl. High temperatures give a severe drop in efficiency, and the presence of a heating regime and lower temperatures give more time to acid scavengers to trap HCl efficiently.

Decomposition of Acid Scavengers and Their Reaction Products

Suppose an unstable acid scavenger decomposes before the “pyrolysis and combustion zone,” or its reaction product decomposes before reaching the test temperature. In that case, we will have an open door allowing HCl to get the bubbling devices. So many common organic acid scavengers used as long-term thermal stabilizers cannot be used as acid scavengers at high temperatures.

2.6. Definition of Efficiency of the Acid Scavenger

O’Mara proposed the Molar Absorption Efficiency (MAE) as a measure of the efficiency of an acid scavenger. MAE is the amount of HCl absorbed divided by the theoretical amount that could be absorbed by each filler [25]. Chandler and others defined efficiency based on the stoichiometry of reaction between CaCO_3 and HCl [14]. For calculating the efficiency of an acid scavenger through [25] or [14], we need to know precisely the reactions of all the involved actors. With multiple-step reactions, this cannot be feasible. It is better to propose a new definition of efficiency, considering not the moles of reactants and products but just the measure of the “effects” of the acid-scavenging reactions, whatever they are. The best candidate is an equation representing the efficiency E as a linear function of pH. Thus, performing EN 60754-2, we can propose Equation (1) as the definition of the efficiency of an acid scavenger at high temperature in the condensed phase:

$$E = 100 \times \frac{(\text{pH} - \text{pHs})}{(\text{pHw} - \text{pHs})} \quad (1)$$

where $\text{pH} \in [\text{pHw}, \text{pHs}]$.

Equation (1) is a straight line, where the measured pH cannot stay outside its “existence region” (pHw – pHs). pHs is the minimum pH reachable when the stoichiometric quantity of HCl reaches the bubbling devices. It is a theoretical value and can be calculated directly from the sources of HCl in the formulation. pHw is the double deionized water (DDW) pH; i.e., the maximum reachable pH when HCl coming from the smoke is negligible. If the measured pH equals pHs , the efficiency is 0%, while if the measured pH equals pHw , the efficiency is 100%.

So, we can quickly get the efficiency of a specific acid scavenger in a single-step reaction or a “team” of acid scavengers in a multiple-step reaction by measuring the pH of the samples and DDW and calculating the pHs of the used formulations.

2.7. The Driving Force of pH and Conductivity in Solution

Reference [17] shows that, in aqueous solutions of HCl at different concentrations, conductivity and pH are linked by Equation (2):

$$c = a \times e^{(-b \times pH)} \quad (2)$$

where a and b are constants.

Suppose the scavenging of HCl is in the condensate phase and the contribution by the evaporation of reaction products is negligible. Performing EN 60754-2, the pH values and conductivities should fit Equation (2) very well. Therefore, ion chromatography (IC) should measure Cl⁻ as the main species, being the concentration of other cations and anions insignificant. In this context, pH can be derived indirectly through IC measurements.

Part III of this paper enters more into the details of this topic, comparing the theoretical values coming from standard solutions of HCl, those calculated by Kohlrausch and Debye–Hückel–Onsager equations, and the experimental data coming from EN 60754-2.

2.8. Impact of Acid Scavengers on Flame Retardancy and Smoke Suppressant Properties

Acid scavengers interfere with the flame retardant mechanism in the gas and condensed phases, inhibiting flame retardancy. References [26–28] show the impact on the Limiting Oxygen Index (LOI) of several calcium carbonates with different particle sizes. In particular, the behavior of 0.1-micron calcium carbonate is better as acid scavengers compared to 14-micros and 1-micron ones. As expected by an inert filler, 14-micron calcium carbonate does not affect LOI, and LOI slightly increases as the filler concentration increases. However, 0.1-micron calcium carbonate is reactive. Getting in HCl with high efficiency, 0.1-micron calcium carbonate reduces LOI up to its stoichiometric value when the exact quantity of CaCO₃ is available for reacting completely with the potentially released HCl. After that, it increases again, behaving as an inert filler. The 1-micron calcium carbonate shows both characteristics; i.e., a constant trend up to stoichiometric value and a slight increase after. All these confirm that the higher the HCl scavenging, the lower the flame retardance. PVC with acid scavengers loses its inherent flame retardance. The scavenging of HCl also interferes with some conventional flame retardants used in PVC. Antimony trioxide (ATO) is a common flame retardant working only in the gas phase through the formation of SbCl₃, trapping the hot radicals feeding the flame [23]. Since SbCl₃ is less volatile than HCl or HBr, it stays longer in the flame, enhancing flame retardancy in PVC compounds. When a powerful acid scavenger at high temperatures is introduced into the compound, all HCl is trapped as chloride in the condensed phase, which prevents the formation of SbCl₃ and the reactions trapping the hot radicals. The consequence is a dramatic LOI drop, as reported in [16–18].

Furthermore, the scavenging of chlorine by acid scavengers interferes with the charring mechanism of some incipient Lewis acids used as flame retardants and smoke suppressants in PVC. Most of these precursors are metal oxides or salts reacting with HCl and yielding chlorides acting as potent Lewis acids. Starnes and co-workers [29,30], Jianqi Wang [31] and Li [32], and Rodolfo and Innocentini-Mei [33] studied some of them. Starnes and others [29,30] claimed the precursor of Lewis acid as an inhibitor of benzene formation from cis-trans polyene sequences to justify the smoke suppressant properties and the flame retardancy of some molybdenum compounds. In Starnes’s theory in [29], Lewis acids seem to advantage parallel reactions, yielding to the production of crosslinked solid char through the following steps: the creation of preferential pathways bringing to

all-trans sequences (Pathways 3 and 4 in Figure 1) and Diels–Alder reactions and Friedel–Crafts alkylations catalyzed by Lewis acid (Pathways 5 and 6 in Figure 1).

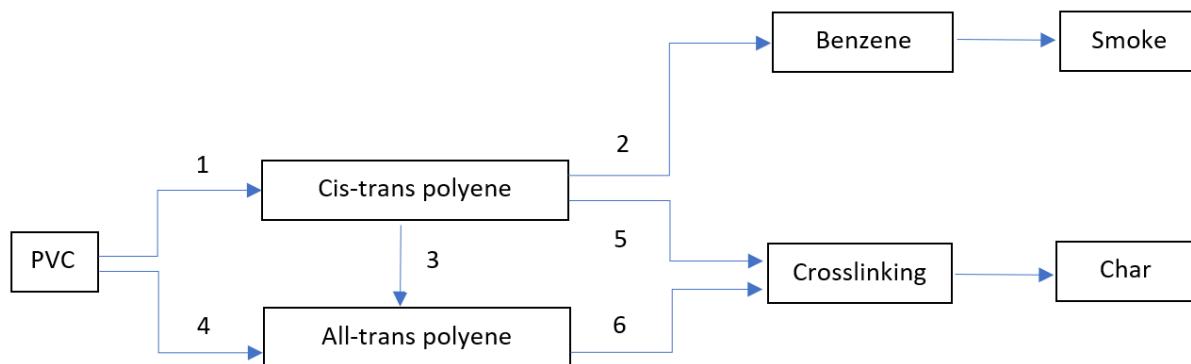


Figure 1. Pathways bringing to char and smoke in PVC combustion.

Without the Lewis acid, benzene is produced following Patterns 1 and 2 in Figure 1. The reaction is an intramolecular cyclization, as described by O’ Mara [34]. Benzene is formed during Stage 1 of the pyrolysis and combustion [24] and is a potent source of soot and smoke during PVC combustion.

Therefore, potent acid scavengers, inhibiting the reactions bringing about the formation of metal chlorides, switch off all pathways yielding the char, causing a substantial release of smoke, as reported in these proceedings [16,17]. All smoke suppressants involving chlorides, acting as Lewis acids promoting char, are, therefore, useless in low-smoke acidity compounds. Even the smoke suppressants avoiding cationic cracking at high temperatures in large fires [35,36] lay in that category. This topic will be discussed in detail in Part IV of the paper.

3. Conclusions

The acid scavenging of HCl at a high temperature can pass through a single-step or multiple-step reaction in which HCl is released and captured by different actors. Multiple-step reactions can be used to get the advantage of synergism capable of increasing the efficiency of the HCl scavenging. An acid scavenger at a high temperature in the condensed phase can fail or succeed, depending on how quickly it reacts with the HCl, the thermal stability of its reaction products, and how fast HCl evolves from PVC. Therefore, the acid scavenger’s chemical nature, the particle size, how much disperses, the test temperature, and the heating regimes affect the efficiency of the scavenging. This topic will be discussed in detail in Part II of this paper.

Particularly, the temperature and heating regimes are critical parameters influencing the scavenging efficiency. Therefore, EN 60754-2 and EN 60754-2 with thermal profiles of EN 60754-1 have been compared in Part V of this paper.

Furthermore, EN 60754-2 is designed for collecting fumes in bubbling devices containing water, and it is strategic to know which species affect the pH and conductivity to “design” a good acid scavenger at high temperatures in the condensed phase. Suppose a mechanism of scavenging in the condensed phase is involved, and the volatility of the reaction products is low. In that case, the pH and conductivity are ruled only by the HCl reaching the bubbling device. IC should find Cl⁻ as the predominant species, ICP and IC should determine the low concentration of all cations in the solution, and pH and conductivity should be linked by the mathematical formulation indicated in (2). This topic will be discussed in detail in Part III.

Lastly, HCl scavenging inhibits radical trapping and interferes with the char mechanisms of the PVC compound in case of fire. Therefore, the low smoke acidity

compound can have less fire performance, with low flame retardance and more dense smoke. This drawback highlights the need to introduce a new generation of flame retardants and smoke suppressants if we want to keep the low smoke acidity, high flame retardancy, and minor smoke release together in a PVC compound. This topic will be discussed in detail in Part IV, where formulations containing potent acid scavengers giving low smoke acidity compounds reduce flame retardance and increase smoke release.

Funding: This research received no external funding.

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement:

Acknowledgments: The author wants to acknowledge Ing. Carlo Ciotti, Ing. Marco Piana, the PVC Forum Italia and the PVC4cables staff, and Emma Sarti for their help and support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hull, T.R.; Stec, A.A.; Paul, K.T. Hydrogen chloride in fires. *Fire Saf. Sci.* **2008**, *9*, 665–676. <https://doi.org/10.3801/IAFSS.FSS.9-665>.
2. Obloj-Muzaj, M. Fire performance of PVC. *Int. Polym. Sci. Technol.* **2001**, *28*, 98–100. <https://doi.org/10.1177/0307174X0102800319>.
3. Hirschler, M. Fire safety, smoke toxicity, and acidity. In Proceedings of the Flame Retardants 2006, London, UK, 14–15/02/2006.
4. ISO/TR 20118:2019; Plastics—Guidance on fire characteristics and fire performance of PVC materials used in building applications 2019; ISO: Geneva, Switzerland. Available online: <https://www.iso.org/standard/67071.html> (accessed on 16 August 2022).
5. Babrauskas, V.; Gann, R.G.; Levin, B.C.; Paabo, M.; Harris, R.H.; Peacock, R.D.; Yusa, S. A methodology for obtaining and using toxic potency data for fire hazard analysis. *Fire Saf. J.* **1998**, *31*, 345–358. [https://doi.org/10.1016/S0379-7112\(98\)00013-7](https://doi.org/10.1016/S0379-7112(98)00013-7).
6. Guillaume, E.; Didieux, F.; Thiry, A.; Bellivier, A. Real-scale fire tests of one-bedroom apartments with regard to tenability assessment. *Fire Saf. J.* **2014**, *70*, 81–97. <https://doi.org/10.1016/j.firesaf.2014.08.014>.
7. Beitel, J.J.; Bertelo, C.A.; Carroll, W.F.; Gardner, R.O.; Grand, A.F.; Hirschler, M.M.; Smith, G.F. Hydrogen chloride transport and decay in a large apparatus I. Decomposition of poly(vinyl chloride) wire insulation in a plenum by current overload. *J. Fire Sci.* **1986**, *4*, 15–41, <https://doi.org/10.1177/073490418600400103>.
8. Babrauskas, V.; Peacock, R.D. Heat release rate: The single most important variable in fire hazard. *Fire Saf. J.* **1992**, *18*, 255–272. [https://doi.org/10.1016/0379-7112\(92\)90019-9](https://doi.org/10.1016/0379-7112(92)90019-9).
9. Babrauskas, V.; Harris Jr, R.H.; Gann, R.G.; Levin, B.C.; Lee, B.T.; Peacock, R.D.; Paabo, M.; Twilley, W.; Yoklavich, M.F.; Clark, H.M. Fire hazard comparison of fire-retarded and non-fire-retarded products (NBS SP 749). In *Special Publication (NIST SP)*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 1988. <https://doi.org/10.6028/NBS.SP.749>.
10. Sarti, G.; Piana, M. PVC in cables for building and construction. Can the “European approach” be considered a good example for other countries? *Acad. Lett.* **2022**, Article 5453. <https://doi.org/10.20935/AL5453>.
11. Greg, S. Quick method for determining the acid gas evolution from PVC formulations. *J. Vinyl Technol.* **1997**, *9*, 18–21. <https://doi.org/10.1002/vnl.730090106>.
12. Sumi, K.; Morwick, D.W. *Acid Gas Evolution from PVC Using DBR/NRC Method*; Internal Report (National Research Council of Canada. Division of Building Research), no. DBR-IR-425; National Research Council of Canada: Ottawa, ON, Canada, 1976. <https://doi.org/10.4224/20338163>.
13. Sze On Chan, H. Measurement of hydrochloric acid emission from burning PVC compounds. *J. Fire Sci.* **1984**, *2*, 106–122. <https://doi.org/10.1177/073490418400200203>.
14. Chandler, L.A.; Hirschler Smith, G.F. A heated tube furnace test for the emission of acid gas from PVC wire coating materials: Effects of experimental procedures and mechanistic considerations. *Eur. Polym. J.* **1987**, *23*, 51–61, [https://doi.org/10.1016/0014-3057\(87\)90098-X](https://doi.org/10.1016/0014-3057(87)90098-X).
15. Sarti, G. How formulations can influence the PVC cables fire behavior. In Proceedings of the 1st PVC4cables Conference, Lyon, France, 26 October 2017. <https://doi.org/10.13140/RG.2.2.19480.03849>.
16. Sarti, G.; Piana, M. New formulations and test comparison for the classification of PVC cables under EU regulation n° 305/2011 for construction products. In Proceedings of the AMI Cables 2019, Duesseldorf, Germany, 5–7 March 2019. <https://doi.org/10.13140/RG.2.2.21736.11528>.
17. Sarti, G.; Piana, M. PVC cables and smoke acidity: A review comparing performances of old and new compounds. In Proceedings of the AMI Cables 2020, Duesseldorf, Germany, 3–5 March 2020. <https://doi.org/10.13140/RG.2.2.15672.26881>.
18. Bassi, I. Characterization of PVC Compounds and Evaluation of Their Fire Performance, Focusing on the Comparison between EN 60754-1 and EN 60754-2 in the Assessment of the Smoke Acidity. Thesis,, University of Bologna, Bologna, Italy, October

2021. Available online: https://www.pvc4cables.org/images/assessment_of_the_smoke_acidity.pdf (accessed on 16 August 2022).

- 19. Sarti, G.; Piana, M. Smoke acidity and a new generation of PVC formulations for cables. In Proceedings of the AMI Formulation 2021, Cologne, Germany, 16–18 September 2021.
- 20. Sarti, G. Developing and improving fire performance and safety in PVC. In Proceedings of the Future of PVC Compounding, Production & Recycling, online, 24–25 February 2022. <http://dx.doi.org/10.13140/RG.2.2.30678.32322>.
- 21. Aupetit, A. Overview of the global cable industry—markets and materials. In *The Global Cable Industry: Materials, Markets*, 1st ed.; Beyer, G., Ed.; John Wiley & Sons Ltd: Chichester, UK, 2021; pp. 1–20. <https://doi.org/10.1002/9783527822263.ch1>.
- 22. Starnes, W.; Xialong, G. Mechanism of autocatalysis in the thermal dehydrochlorination of poly(vinyl chloride). *Macromolecules* **2004**, *37*, 352–359. <https://doi.org/10.1021/ma0352835>.
- 23. Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J.M.; Dubois, Ph. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Mater. Sci. Eng. Rep.* **2009**, *63*, 100–125. <https://doi.org/10.1016/j.mser.2008.09.002>.
- 24. Wu, C.H.; Wu, C.H.; Chang, C.Y.; Hor, J.L.; Shih, S.M.; Chen, L.W.; Chang, F.W. Two-stage pyrolysis model of PVC. *Can. J. Chem. Eng.* **1994**, *72*, 644–650. <https://doi.org/10.1002/cjce.5450720414>.
- 25. O'Mara, M.M. Pyrolysis–gas chromatographic analysis of poly(vinyl chloride). II. In situ absorption of HCl during pyrolysis and combustion of PVC. *J. Polym. Sci. Part A-1 Polym. Chem.* **1971**, *9*, 1387–1400. <https://doi.org/10.1002/pol.1971.150090519>.
- 26. Brown, S.K.; Martin, K.G. Toxic gas and smoke measurement with the British Fire Propagation test. III: UPTV formulations with reduced HCl evolution. *Fire Mater.* **1985**, *9*, 95–102. <https://doi.org/10.1002/fam.810090208>.
- 27. Matthews, G.; Plumper, G.S. Effects of calcium carbonate fillers on the behaviour of PVC in fires. *Br. Polym. J.* **1981**, *13*, 17–21. <https://doi.org/10.1002/pi.4980130105>.
- 28. Matthews, G.; Plumper, G.S. Effects of fillers on and the role of hydrogen chloride in the behaviour of PVC in fires. *Br. Polym. J.* **1984**, *16*, 34–38. <https://doi.org/10.1002/pi.4980160107>.
- 29. Starnes, W.H.; Wescott, L.D.; Reents, W.D.; Cais, R.E.; Villacorta, G.M.; Plitz, I.M.; Anthony, L.J. Mechanism of poly(vinyl chloride) fire retardance by molybdenum(vi) oxide. Further evidence in favor of the lewis acid theory. In *Polymer Additives. Polymer Science and Technology*; Kresta, J.E., Ed.; Springer, Boston, MA, USA, 2007; Volume 26, pp. 237–248. https://doi.org/10.1007/978-1-4613-2797-4_18.
- 30. Starnes, W.H., Jr.; Edelson, D. Mechanistic aspects of the behavior of molybdenum (VI) oxide as a fire-retardant additive for poly (vinyl chloride). An interpretive review. *Macromolecules* **1979**, *12*, 797–802. <https://doi.org/10.1021/ma60071a001>.
- 31. Li, B.; Wang, J. A cone calorimetric study of flame retardance and smoke emission of PVC. I. The effect of cuprous and molybdc oxides. *J. Fire Sci.* **1997**, *15*, 341–357. <https://doi.org/10.1177/073490419701500501>.
- 32. Li, B. A study of the thermal decomposition and smoke suppression of poly(vinyl chloride) treated with metal oxides using a cone calorimeter at a high incident heat flux. *Polym. Degrad. Stab.* **2002**, *78*, 349–356. [https://doi.org/10.1016/S0141-3910\(02\)00185-4](https://doi.org/10.1016/S0141-3910(02)00185-4).
- 33. Rodolfo, A.; Innocentini Mei, L.H. Metallic oxides as fire retardants and smoke suppressants in flexible poly(vinyl chloride). *J. Appl. Polym. Sci.* **2010**, *118*, 2613–2623. <https://doi.org/10.1002/app.32596>.
- 34. O' Mara, M.M. Combustion of PVC. *Pure Appl. Chem.* **1977**, *49*, 649–660. <https://doi.org/10.1351/pac197749050649>.
- 35. Zestos, A.G.; Grinnell, C.L.; Vinh, L.J.; Pike, R.D.; Starnes, W.H., Jr. Metal-exchanged clay and zeolite additives as smoke suppressants and fire retardants for poly(vinyl chloride). *J. Vinyl Addit. Technol.* **2009**, *15*, 87–91. <https://doi.org/10.1002/vnl.20179>.
- 36. Starnes Jr, W.H.; Pike, R.D.; Cole, J.R.; Doyal, A.S.; Kimlin, E.J.; Lee, J.T.; Murray, P.J.; Quinlan, R.A.; Zhang, J. Cone calorimetric study of copper-promoted smoke suppression and fire retardance of poly(vinyl chloride). *Polym. Degrad. Stab.* **2003**, *82*, 15–24, [https://doi.org/10.1016/S0141-3910\(03\)00158-7](https://doi.org/10.1016/S0141-3910(03)00158-7).