Transport and Decay of Combustion Products in Fires

by

M.M. Hirschler and F.M. Galloway
(GBH International, Mill Valley, CA, US)

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Marcelo M. Hirschler and F. Merrill Galloway, Jr.
GBH International, US

ABSTRACT

The decay of hydrogen chloride (HCl) has been studied in a variety of large scale and small scale fire scenarios. In fact, it has also been studied in scenarios where HCl was not generated in a fire but was simply introduced into the scenario directly. The effects of a variety of atmospheric conditions and of surfaces (in particular, but not only, construction surfaces) have also been investigated. The large scale scenarios were principally the following: (a) a room and plenum, where HCl was generated in the plenum by electrical overload of poly(vinyl chloride) (PVC) wire and cable coatings, (b) room and corridor, where HCl was generated in a "fire" room and followed along a corridor, (c) room-corridor-room, where HCl was generated in a "fire" room and followed along a corridor into a "target" room and (d) HVAC scenario, where HCl was injected into a long series of tunnels simulating a heating, ventilating and air conditioning system. The small scale scenarios involved box-like containers, with 3 L and 200 L volumes, as well as heated glass flasks, of spherical and cylindrical shapes.

The surfaces studied included the following: poly(methyl methacrylate) (PMMA), glass, gypsum board, cement, Marinite, ceiling tile, painted gypsum board, painted PMMA and soot. The other conditions investigated included temperature, humidity and presence or absence of a variety of fluids. In view of the very rapid HCl decay in most of those surfaces, the effects were often studied with small "chips" of materials in a PMMA chamber, with fresh walls for each experiment. Experiments were also done to investigate the effect of surface ageing, with painted gypsum board, painted PMMA and unpainted gypsum board walls.

As a result of all of this experimental work, a model was developed and gradually improved, to be able to predict HCl generation and decay under all conditions able to be anticipated. The initial model was based on mathematical correlations starting with experimental data. Eventually, the model contained scale-independent parameters for all the surfaces used. Fitting these parameters to the small scale data allowed generalization of the results to scenarios of all scales.

The HCl generation and deposition model was also included by NIST into their Hazard I zone fire model and this was also analyzed by conducting a background and a technical review of this capability, including: (1) guidelines for simulating HCl generation, (2) the surfaces for which the parameters needed for modeling currently exist and (3) the importance of humidity in the deposition process. The HCl generation and decay model from version 1.1 of Hazard 1 was applied to the full scale tests and the results compared to the experimental data, showing excellent agreement. A demonstration run was also made, showing the predictive power of the HCl capability, in a realistic fire scenario (two-story home). The HCl decay model showed how HCl levels are much lower, particularly remote from the fire, than would have been the case if HCl had not undergone decay.

This work shows that HCl transport and decay is an important phenomenon that must be applied whenever investigating fire hazard and that the model generated is robust enough that it can be applied to a number of scenarios where HCl is present, whether PVC is or is not present. Thus, both the

phenomenon of HCl decay and the associated model are of particular importance in fire hazard assessment.

INTRODUCTION

The problem of assessing the fire hazard of a material is a composite of three separate aspects:

(1) The generation of heat and combustion products from a material when it burns;
(2) The transport of heat and of fire gases and particulates to the vicinity of the building occupant; and
(3) The response of each individual subject to specific insults (thermal, toxic and visual).

The phenomenon of generation is associated with a variety of factors, including the ignitability of the material and properties of the burning material such as the associated flame spread, its rate of heat release, total amount of heat released and the type and amount of combustion products released from it.

The phenomenon of transport is generally treated as a buoyancy-driven multi-room problem of gas and heat dynamics, often by means of zone-type fire models (such as the FAST model [1], the Harvard Code [2] or the OSU Code [3]). The majority of common combustion products [4, 5] are sufficiently unreactive so that their chemistry during transport is of minor importance compared to the generic aspects of heat and mass transport. The most important compound that is an individual exception to this rule is hydrogen chloride, a very reactive common combustion product which has been shown to decrease in concentration (decay) by deposition [6-23]. The density of smoke, as well as various characteristics of the soot particles contained in it, can also be altered by the entrainment of air into the mixture of combustion products.

The phenomenon of response to an insult also contains several aspects. These include the effects of high temperatures, of thermal radiation, of lack of visibility, and of the toxic potency of individual components of the smoke and their potential interactions. In the present connection it is of particular interest to discuss the aspect of hydrogen chloride (HCI) decay, which is important for assessing actual fire hazard. The hygroscopic nature of HCI is well known and this has always suggested that its presence in a fire atmosphere might be rather transient. Furthermore it has generally been found difficult to recover all of the HCl evolved into an atmosphere, even in small equipment [6]. The evidence for HCI decay ranges from early work in a smoke chamber similar to that in the NBS smoke chamber (ASTM E 662) [8] to animal toxicity experiments carried out in a standard size room [18]. There have also been series of experiments involving room/plenum [18-19] and room/corridor configurations [23]. In all cases the peak concentration of HCI measured has been much lower than the theoretical value obtained from the chlorine content of the material decomposed. Furthermore, this HCI concentration soon decreases to a very low value. It has been shown too that the presence of water enhances decay [13-16, 19-23] as does, particularly, the presence of sorptive surfaces.

Some of that work has been analyzed by using various means of parameterization of the results [20-24]. This approach has the advantage of yielding rapid information on the effect of the variables involved. It has, however, the disadvantage that the model involved is not general enough to be applied to situations other than the specific ones for which it has been designed.

Eventually, in 1987, a model for HCI generation, transport, and decay was presented [25] that is consistent with the general zone fire models, in particular FAST [1]. The 1987 model [25] is, of course, a zone model, where the standard engineering approach to be taken is that of having "lumped" parameters rather than "distributed" parameters. In other words there is integration over space so as to maintain the temporal dependency (to show the variation of concentration with time), while becoming spatially independent. The basic model assumes well-mixed layers for all compartments (within the smoke layer); mass transfer coefficients (estimated using the same approach as is used for convective heat transfer in

fire models) for transport of HCI from its source, i.e. the hot smoke layer, to the surface where it will decay; partition coefficients for representing gas-solid equilibria at the surface; and a combination of diffusion into a surface and reaction with the surface for the decay on any surface.

The 1987 model [25] was, in the first instance, applied to data obtained in small-scale experiments [19-20, 22], in order to obtain surface specific parameters describing the decay process, and the results were then used to predict the behavior in large-scale experiments [18, 23-24].

EARLY SMALL SCALE EXPERIMENTS

The first series of experiments conducted to develop this decay model was associated with a fire involving the thermal decomposition of poly(vinyl chloride) (PVC) electrical insulation materials by electrical overload [18]. The burns were conducted in an 180 L poly(methyl methacrylate) (PMMA) chamber, like the one used in the ASTM E 1678 or NFPA 269 smoke toxicity test. The amount of wire insulation used represented loadings of 22.4, 44.7 and 89.4 mg/L in the chamber. The wire was placed on a porous surface (Kaowool) to prevent loss of material due to melting. HCl concentrations were assessed by several methods. The results indicated that the concentration of HCl emitted from the decomposition of PVC passed through a maximum and then decreased. They also showed that the maximum concentration of HCl measured was less than 40% of the amount that should have been measured based on the chlorine content of the PVC. This was the first clear indication of HCl decay. The rate of HCl decay was fast at the beginning of the fire but gradually decreased as the HCl concentration reached an asymptotic value. It was not until HCl had already started to decay that any of the other combustion products (carbon monoxide, carbon dioxide, total hydrocarbons) reached their peak values. The peak concentrations of all products other than HCl were able to be clearly associated with the fuel chemical composition.

The next set of small-scale experiments involved studying the effects of surfaces on HCl decay in a small 3 L box, lined with various construction materials, namely gypsum board, painted gypsum board, ceiling tile, cement block, Marinite, PMMA and painted PMMA [21]. The paint involved two layers of white latex paint. The box was evacuated and purged with either dry air or air at certain pre-set humidities. Then, HCl was injected with a syringe and the atmospheric concentrations were measured in the box (in some of these experiments forced convection was used, to enhance mixing). The decay of HCl occurs in two stages: (a) a very fast (almost instantaneous) decay) and (b) an exponential, first order, decay as shown in Equation (1):

$$\ln [(C_0 - A_0 /C] = k\, t$$

where C_0 is the concentration of HCl injected into the chamber(in ppm), C is the concentration (also in ppm) at time t (in min) and A_0 and k are the pre-exponential parameter and the rate decay constant. The calculation of parameters was done by non linear curve fitting. Results are shown in Table 1. They indicate the following:

(1) The rate of decay (as evidenced by the rate decay constant k) decreases as the surface gets re-used;
(2) Different surfaces have different effects, with PMMA being very inefficient in causing HCl decay, while cement block, Marinite, unpainted gypsum board and ceiling tiles are extremely efficient;
(3) Painting a surface affects its capability of causing HCl decay so that painted PMMA is much more effective than plain PMMA while painted gypsum board is much less effective than unpainted gypsum board;
(4) Painted surfaces behave in a manner strongly affected by the paint itself; and
(5) Humidity strongly enhances decay.

Figure 1 shows how the efficiency of surfaces to enhance decay is in the following order (note that the vertical axis for unpainted gypsum board is different than the one for the painted surfaces):

Painted PMMA < Painted gypsum board < Unpainted gypsum board

Figure 2 shows that the effect of humidity on painted gypsum board is to increase decay rates

LARGE SCALE EXPERIMENTS

Room-plenum scenario

The small-scale experiments on wire discussed earlier were preliminary to the first set of large-scale experiments involving 9.14 m of PVC-coated building wire [18-20]. The wire was laid on the floor of a simulated plenum above a room. The dimensions of the plenum were 2.4 x 3.7 m, with a 1.2 m height, and it had painted gypsum board walls and ceiling and ceiling tile floor. The floor of the simulated plenum was simply covered by ceiling tiles laid on metal tracks, above a standard room (3.7 x 2.4 x 2.4 m). The decomposition of the wire was done at currents of 180 - 250 A.

During these tests it could be shown that the effectiveness of the experimental measurement process was very good, so that it would have been expected that the vast majority of the HCl present in the atmosphere would have been measured. In fact, however, the peak concentrations of HCl measured represented only less than 35% (actually 21-33%) of the stoichiometric chlorine content in the "fuel". Moreover, measurements made on the ceiling tiles (which were the floor of the plenum and the ceiling of the room) showed very high chlorine content, so that a mass balance resulted in virtually complete accounting of the original chlorine.

There was virtually no transport of HCl into the room below the plenum, but there was significant transport downward of both carbon monoxide (CO) and hydrocarbons (CHx), as well as of carbon dioxide. These latter gases showed 10-20% of their maximum concentration in the room below the plenum, while HCl showed less than 3% after 30 minutes, even in the plenum, and most of it ended up in the ceiling tile and gypsum board surfaces. Moreover, considerable amounts of HCl initially decayed very rapidly, just as in the small scale experiments, while the other gases measured did not. The slight decrease in CO and CHx concentrations is due to the diffusion to the outside occurring through small leaks in the room and plenum outer surfaces. Figure 3 shows these effects.

A rough analysis of these data indicates that HCl disappears from the atmosphere at a rate of up to 270 ppm/min (based on peak concentrations), which corresponds to a first order half-life of some 7 minutes. This means that a very large proportion of the HCl generated disappeared before the other key combustion product gases achieved peak concentrations. In particular, within the time frame of typical fires, say 30 minutes, the HCl concentration will have both peaked and decayed to less than 25% of its maximum value.
Subsequent analyses of the room-plenum experiments [19] showed that the kinetics of the reactions can be captured by the following model:

Potential HCl in PVC → Atmospheric HCl ↔ Deposited HCl ,

where a rate constant applies for each equation (k_{12} for the dehydrochlorination [first equation], k_{23} for the deposition of HCl [second equation, forward direction] and k_{32} for the desorption [second equation, backward direction]).

Table 1 - Kinetic HCl decay parameters of surface exposures

Surface Material	Conditions Initial HCl (cm^3)	T (K	Water (%)	k (min^{-1})	A_0/C_0) (-)	Note
Virgin wall materials						
PMMA	3	298	0	0.008	0.21	
Painted PMMA	7	297	0	0.110	0.45	
Painted gypsum board	5	355	0	0.69	0.59	
Ceiling tile (back)	7	373	0	ca. 2	ca. 0.5	
Cement block	7	470	0	3.3	0.92	
Ceiling tile (front)	7	373	0	> 5	ca. 0.75	
Unpainted gypsum board	7	373	0	5.9	0.24	
Cement block	3	357	0	> 8	ca. 0.75	
Marinite	7	373	0	> 12	ca. 0.75	
Re-use of wall materials						
Painted PMMA	7	297	0	0.110	0.45	a
Painted PMMA	7	297	0	0.036	0.44	
Painted PMMA	7	298	0	0.025	0.40	
Painted PMMA	7	297	0	0.020	0.30	
Painted PMMA	7	297	0	0.020	0.44	
Painted PMMA	7	297	0	0.014	0.36	
Painted PMMA	7	297	0	0.013	0.44	
Painted PMMA	7	296	0	0.014	0.34	
Painted PMMA	7	298	0	0.013	0.31	
Painted gypsum board	3	350	0	1.14	0.59	a
Painted gypsum board	3	352	0	0.69	0.42	
Painted gypsum board	3	352	0	0.50	0.37	
Painted gypsum board	3	353	0	0.29	0.58	
Painted gypsum board	3	355	0	0.26	0.44	
Painted gypsum board	7	357	0	0.30	0.49	
Painted gypsum board	3	351	0	0.34	0.54	
Painted gypsum board	3	352	0	0.31	0.48	
Painted gypsum board	3	353	0	0.27	0.47	
Painted gypsum board	3	354	0	0.31	0.46	
Unpainted gypsum board	7	373	0	5.94	0.24	a
Unpainted gypsum board	7	373	0	5.37	0.11	
Unpainted gypsum board	7	376	0	4.02	0.37	
Unpainted gypsum board	7	375	0	4.81	0.30	
Unpainted gypsum board	7	373	0	4.58	0.31	
Unpainted gypsum board	7	375	0	4.25	0.25	b
Unpainted gypsum board	7	373	0	3.45	0.31	b
Unpainted gypsum board	7	373	0	1.09	0.67	b
Unpainted gypsum board	10	373	0	2.07	0.49	c
Unpainted gypsum board	10	373	0	3.83	0.56	
Effect of humidity						
Painted gypsum board	3	321	0.0	0.42	0.85	a
Painted gypsum board	3	324	0.0	0.44	0.53	
Painted gypsum board	3	324	3.0	0.49	0.40	
Painted gypsum board	3	324	5.0	1.64	0.81	
Painted gypsum board	3	355	1.5	0.52	0.87	
Painted gypsum board	3	355	3.0	0.94	0.75	
Painted gypsum board	3	354	5.0	1.23	0.59	

a: Test on surface used for first time - subsequent tests re-use same surface
b. 200 cm^3 of HCl injected before test and box was purged
c: 99 g of HCl injected before test and box was not purged

The rate constants, which could be used to fit the data very well, showed that the dehydrochlorination reaction was the fastest of the three, followed closely by the deposition reaction (both of them with rate constants of 0.12-0.36 1/min), while the desorption reaction was extremely slow (rate constants in the order of 0.005 1/min). The rate of desorption is slightly higher in the presence of a very non sorptive surface such as PMMA (which is not a construction surface): 0.011/min).None of the construction surfaces assessed (Marinite, gypsum board, ceiling tile, mineral fiber, cement block and painted gypsum board) gave such high desorption rate constants. Interestingly, higher humidity enhances considerably the rate of HCl decay but also enhances slightly the rate of HCl desorption from construction surfaces.

The analysis of the room-plenum experiments showed that virtually all the chlorine in the "fuel" could be accounted for in the experiments, with the following disposition:

Chlorine fate: 53% walls, 25% char, 19% ceiling tiles and 3% filters.

Room-corridor scenario

In these experiments [26], a standard rigid PVC (containing nothing more than 2 wt% of processing aids) was fabricated into 30 cm square plates, 0.22 cm thick, so that a mass of ca. 500 g (actually 400-600 g) of PVC was exposed. A test scenario was built with a standard burn room (3.7 m x 2.4 m x 2.4 m high), connected by a doorway to a 19 m long corridor. The corridor was closed off at the end closest to the burn room and was open on the other end. The room and corridor were all built with painted gypsum board walls. The fire source was a set of three burners forming a 30 cm x 30 cm radiant panel, generating 2.7 MW, with a small gas-fed pilot flame (174 W) and a sand box radiant methane burner, identical to the one in the NFPA 286 room-corner test [27] and set at 5.8 MW. The gas flame was used to ensure that flaming combustion occurred. All experiments lasted 30 minutes and there was no forced convection, other than that generated by the fire itself. HCl concentrations were measured in the burn room doorway and along the corridor. Fresh surfaces were used in each experiment. In the experiments where the thermal input was very small (8 kW) HCl decay was relatively small, because of several factors: (a) low smoke flow rates, (b) very low entrainment levels, (c) lower temperatures and (d) the fact that there was an unrealistically low probability of the smoke flow from reaching a surface on the corridor end (which had no doorway). The experiments where the methane burner operated at 40 kW and 200 kW showed much higher levels of decay. It is worth noting, as will be discussed later, that the data and the 1987 HCl decay model [25] show good correlation.

Room-corridor-room scenario

In these experiments [28], the same type of PVC as in the room-corridor scenario experiments was used. The amount of PVC used per test was in the order of ca. 1,900 g. The room was also identical to the one in the room-corridor scenario, but the corridor was slightly longer (26 m) and, critically, had two features which differed from the room-corridor scenario. They were: (a) a target room, identical in dimensions to the burn room, at the other end of the corridor, with a doorway between it and the corridor and (b) the corridor ended in a wall with a standard doorway. In three of the experiments the HCl was generated by burning PVC and using the same burners as in the room-corridor scenario. In other experiments HCl was introduced directly into the "burn room". HCl concentrations were measured in the burn room, burn room doorway, along the corridor and in the target room. Fresh surfaces were used in each experiment. It was, once more, found that a very large fraction of the HCl was deposited on the walls, built of painted gypsum board. The decay of HCl found in this work was consistent with what had been found in earlier work, and showed that there is almost no decay in the burn room, but that decay along the corridor ranges from 10% (at the doorway) to 30% (at the end of the corridor). Much more significant even is the decay in the target room, where the differences between the expected concentration (i.e. the HCl concentration resulting from no HCl decay) and the actual concentration ranges between 60% and 90%. It needs to be pointed out too that the expected concentration in the target room (and even along the corridor) is not that associated with

100% stoichiometry since the effects of entrainment and dilution of smoke must be taken into account. Thus, for example, in one experiment the burn room concentration reaches an expected peak of ca. 1,500 ppm after a few minutes [from burning almost 2 kg of PVC], but is down to ca. 900 ppm after 30 minutes. The actual concentration measured in the target room reaches a peak of less than 450 ppm (after 15 minutes) and rapidly decays from there. This value is ca. 60% lower than the predicted peak HCl concentration based purely on entrainment and smoke dilution. Figure 4 shows how, for two experiments (one with burning PVC and one directly injecting HCl), the decay is considerable and it can be modeled satisfactorily using the 1987 model [25] formulation.

HVAC scenario

In these experiments [29], the transport and decay of HCl was studied in a simulated heating, ventilating and air conditioning (HVAC) system. The scenario involved a system with 8 sections of an HVAC system, each one 15.24 m long and 0.305 m wide, with the total width of the system being 2.44 m. In this way, the air/stream (or smoke stream, including HCl) is injected with an air blower in one end and exits the other end, into exhaust, after going through all eight sections ad reaching walls at each turn. Four experiments were conducted. In the first two, the first five sections had surfaces composed of painted gypsum board, while the last three sections were built of unpainted gypsum board. In the other two tests, the walls and ceiling of the first five sections were made of PMMA, with the floor still painted gypsum board and the last three sections were made again of unpainted gypsum board. All the painted sections were replaced after each run. The HCl was injected from a cylinder, at a rate controlled via a load cell. The first three experiments were run for 30 minutes and the last one for 22 minutes. HCl concentrations were measured at several distances from the entrance of the duct. In all of the cases there was virtually no HCl remaining and exiting at the HVAC exhaust in spite of HCl concentrations of up to > 4,000 ppm at a distance of 3 m into the HVAC. It is very noticeable how the rate of HCl decay is much lower in runs 3 and 4, where PMMA surfaces are used than in the two earlier runs. For example, at 50 m, there is very little HCl left after the initial two tests (see Figure 5), but it takes a distance of almost 100 m before the HCl gets down to those levels in the last two tests (see Figure 6).

LATER SMALL SCALE EXPERIMENTS

A number of experiments were conducted in small scale equipment [30-33], and analyzed together with the small scale experiments discussed above [18, 21]. The key issue was to try to investigate separately the generation and the decay aspects. In a set of 36 experiments, HCl was generated under conditions of forcefully minimized decay (experiments labeled as "HCl generation without decay", GWD) [30]. The HCl was generated in three glass reactors (two spheres: 12.7 L and 13.1 L in volume, and a 7 L tubular reactor), with walls heated by means of heating tape. The HCl was generated through electrical decomposition of PVC wire coating with copper or carbon steel wire, under well-stirred conditions. Efforts were thus made to minimize the amount of HCl decay so that the decay rate remained much smaller than the generation rate. These experiments were used to create a model for generation of HCl from PVC, based on physico-chemical principles and on the temperature-time pattern measured. This model was, thus, only partly empirical, and replaced a previous model, purely empirical. The model results were employed to obtain a very adequate fit of the entire set of experiments. The results were also used to determine the effects of two different types of metal wire (copper and carbon steel) on the HCl decay rate. Results of the new experiments were also fitted in conjunction with those of earlier experiments, in a larger reaction chamber. This was done in order to verify that the new overall model is, indeed, a good representation of the entire process and it provided an independent confirmation of the validity of the total model for HCl generation, transport and decay reported previously. In another set of tests, a total of 63 experiments were carried out in a 200 L PMMA chamber, wherein a large amount of HCl was injected in the absence and presence of various fluids and surfaces [31]. These experiments were labeled as "HCl decay without generation" (DWG). The fluids used were: water, ethylene glycol, ethylene glycol/water 50/50 mixture, a model for airborne smoke particulates (and several partial models

for such synthetic smoke) and mineral oil. The interior surfaces used for the chamber were PMMA (no added surface), painted gypsum board, ceiling tile and soot. These results showed the efficiency of many fluids as sinks for HCl, with water and synthetic smoke being the most effective. The previously developed 1987 model for HCl transport and decay [25], based on parameters obtained from experiments with HCl formation from PVC combustion or pyrolysis, was used to predict the results, in order to confirm whether a model based on HCl generation from PVC could be applied to cases where no PVC was present. The correlation between experimental and predicted atmospheric HCl concentrations, without fitting any new parameters, was excellent, indicating that the model is robust enough that it can be applied to a number of scenarios where HCl is present, irrespective of its origin.

In the GWD experiments close to 100% of the theoretical amount of HCl was found in the tests, indicating that HCl decay is, indeed, minimal on hot glass walls. Another finding was that ambient temperature significantly affects both the generation and the decay rates of HCl. It was also found that the mode of generation (steel or copper wire) affected the generation and decay: copper is much more reactive than carbon steel. In fact, the presence of even a small amount of wire (either copper or steel) will noticeably increase the rate of HCl decay when other surfaces are non sorptive (PMMA or glass). However, the effect of a small copper wire is dwarfed in practical applications by most construction surfaces, including painted gypsum board, due to the differences in surface area. Table 2 shows the HCl decay rates at various surfaces.

Table 2 - Rates of HCl decay on various surfaces

Surface	**(mol cm^{-2} x 10^{6})**
Copper	21
Carbon steel	2.6
PMMA	0.036
Painted gypsum board	0.78
Ceiling tile	5.3
Cement block	4.4

[HCl]: 4,000 ppm @ 27% Relative humidity and 40ºC
Metal surfaces @ 800ºC - other surfaces @ 27ºC

The study of various surfaces [32] showed that, for unexposed nonmetallic surfaces, HCl decay is faster on unpainted gypsum board (with a half life of less than 1 minute) than on painted gypsum board (half life in the range of 1-2 minutes). HCl has an almost 10-fold longer half life on painted PMMA than on painted gypsum board, with the half life on unpainted PMMA 2-3 times longer still. There is a non-linear effect of repeated exposures to HCl for both painted gypsum board and painted PMMA, but repeated exposure to HCl has no effect on HCl decay on unpainted gypsum board, at least up to 10^{-6} gmol HCl/cm^2 (which is equivalent to 10,000 ppm of HCl initially in the gas phase). In fact, unpainted gypsum board shows essentially no effect up to well over 1% HCl concentration (unrealistically high).

MODELING

The 1987 model [25] developed for HCl generation and decay was incorporated into version 1.1 of the NIST HAZARD I room fire model [34-37]. From the beginning of the modeling work, the intent had always been to formulate the model in a manner consistent with the treatment of convective heat transfer in multi-compartment fire models, particularly FAST [38], a component of HAZARD I. This would, ultimately, allow the HCl transport and decay model to be incorporated into such models. This

section [37] reviews the technical basis of the HCl generation and decay model, shows its validity by comparing computational results with data generated in two full scale fire tests, and then demonstrates its usage in a hypothetical private residence fire scenario. Finally, it provides some guidelines for use of the model in the context of HAZARD I. The first concern is that HCl has not been included in the tenability calculations. Thus, the use of HAZARD I for fires where HCl is a major combustion product must be restricted to the use of FAST, a subsection of HAZARD I. The next overall concern is that the initial ambient humidity, as calculated by the software, is much higher than is realistic. This will cause predictions of excessive HCl decay, and can be solved very easily by the developers of the HAZARD I software. The HCl generation and decay model has been applied to several full scale tests, in room-corridor-room and room-plenum scenarios. The results are compared to the experimental data, to earlier predictions, obtained by using the HCl deposition model and FAST separately, and to the results to be obtained in the absence of HCl decay. Also, a demonstration run is made, showing the predictive power of the HCl capability, in a realistic fire scenario (two story residence). The HCl decay application in HAZARD I showed how HCl levels are much lower, particularly remote from the fire, than would have been the case if HCl had not undergone decay. The overall results of this analysis indicate that the version of HAZARD I released is an excellent first step in the use of the HCl decay and generation model. However, a few difficulties still exist. Some of them are easily solvable (e.g. the overall wall surfaces present) while some others are more inherent in the method (e.g. no deposition on floors).

Model Description

The model for HCl decay during the transport of fire gases assumes: that the HCl concentration is uniform in the bulk gas phase, that transport across the gas boundary layer is described by a mass transfer coefficient, and that partitioning of HCl at the gas/wall interface is described by a surface specific equilibrium coefficient. The rate of disappearance of HCl into the wall is described by a first order rate constant which is specific to the surface material. In most applications of the model, the experimental layout permits the approximation that large surface areas can be treated uniformly, e.g., the entire ceiling in a room. Thus, the model can be formulated in terms of ordinary differential equations with time as the independent variable. This treatment is consistent with "zone modeling" of convective heat transfer in multi-compartment fire models.

Mathematical Formulation

The gas transport equation for HCl is shown in Equation (1)

$$\{d[HCl]\}/\{dt\} = - kc * A * ([HCl] - \{[HCl]_w\} / \{Ke\}) \qquad (1)$$

where the left hand side represents the rate of HCl gas phase concentration change, and the right hand side represents the rate of HCl transfer from the gas to the wall. The variable A represents the area of the surface where the decay is taking place. The constants kc and Ke are the mass transfer coefficient through the gas phase and the HCl partition coefficient (equilibrium constant) between the wall and the gas phase. The calculation of flows in and out of every compartment is not explicitly shown in Equation (1), but is calculated by FAST. The mass transfer coefficient, kc, has units of distance/time. In general, it is a function of the local velocity field and the diffusivity of the transferring species. The similarity of convective mass and heat transfer has been known in the field of transport phenomena for a long time. In its simplest form, this similarity can be expressed as a relation between the convective heat and mass transfer coefficients, known as the Reynolds analogy [36]. Fire driven flows generally meet the conditions assumed in the "Reynolds analogy". Thus, in the FAST implementation of the HCl transport and decay model, the "Reynolds Analogy" is used to obtain kc from the convective heat transfer coefficient. It has been shown that, in most practical situations, the decay rate of HCl from fire gases is

not very sensitive to the convective mass transfer rate [37]. The predicted values of kc should, therefore, be sufficiently accurate in the great majority of cases.

The wall conservation equation for HCl is shown in Equation (2):

$$\{d[HCl]_w\}/\{dt\} = kc * ([HCl] - [HCl]_w/Ke) - kr * [HCl]_w \quad (2)$$

where the left hand side corresponds to the HCl surface concentration rate of change, the first term on the right hand side is the rate of transfer of HCl from the gas to the wall, and the second term is the rate of HCl disappearance of HCl into the wall (first order kinetics). The equilibrium gas concentration at the gas/surface interface (which is not explicitly calculated) is given by equation (3):

$$[HCl]_i = [HCl]_w / \{Ke\} \quad (3)$$

In general, Ke and kr are functions of temperature, humidity and HCl concentration, as well as the specific type of surface material. The effect of water (humidity) is to increase the number of surface sites available for HCl adsorption, leading to the functional form for the effect of water on HCl adsorption shown in Equation (4) i.e.:

$$Ke = F1([HCl], T) * F2([H_2O]) \quad (4)$$

where F1 represents the partition coefficient at zero humidity, as shown in equation (5):

$$F1 = \{b1 * e^{(12500/R*T)} * [HCl]\} / \{1 + b2 * e^{(12500/R*T)} * [HCl]\} - \quad (5)$$

In the case of painted gypsum board, the constants are:

$$b1 = 0.063 \text{ m} \quad \text{and} \quad b2 = 192 \text{ m}^3/\text{kg}.$$

At the other extreme, when the HCl-H_2O binary reaches saturation conditions in the gas phase, any surface will have an infinite capacity to adsorb HCl. There are, thus, two limiting conditions for F2, as shown in Equation (6):

$$F2(0) = 1; \; F2([H_2O]_s) \rightarrow \infty \quad (6)$$

With these limiting conditions, the final form for F2 is shown in Equation (7):

$$F2 = 1 + \{b5 * [H_2O]^{b6}\} / \{([H_2O]_s - [H_2O])^{b7}\} \quad (7)$$

The fitted values for the constants b5, b6 and b7, as well as the constants b1 through b4, for the key construction surfaces used in the HCl decay and generation experiments are shown in Table 3.

Table 3. Surface Coefficients for HCl Decay							
Surface	b1	b2	b3	b4	b5	b6	b7
	(m)	(m^3/kg)	(1/s)	a	b	(-)	(-)
Painted Gypsum	6.3E-03	191.8	0.0587	7476	193	1.021	0.431
PMMA	9.6E-05	0.0137	0.0205	7476	29	1.0	0.431
Ceiling Tile	4.0E-03	0.0548	0.123	7476	30	1.0	0.431
Cement Block	1.8E-02	5.48	0.497	7476	30	1.0	0.431
Marinite	1.9E-02	0.137	0.030	7476	30	1.0	0.431
a: (J/ g mol); b: $(m^3/kg)^{(b7-b6)}$							

The expression for the saturation concentration of water, $[H_2O]_s$, was developed by linear regression of "data" points generated from a rigorous vapor/liquid phase dissociation equilibrium model for the HCl-water system. Equation (8) shows how to calculate the saturated water concentration from polynomial expressions. These expressions are 5th order in [HCl], 3rd order in temperature and also contain combined temperature/concentration terms, all of which are a function of ambient temperature.

$$[H_2O]_s = \{0.556 * 10^{-4} * (\text{Polynomial Expression})\} / \{R * T\} \quad (8)$$

The term kr in equation (2) is the coefficient for the decay rate of HCl on the surface, which is assumed to be a first order process in the surface concentration $[HCl]_w$. Previously kr was assumed to be a constant independent of temperature, with a different value for each type of surface. However, when investigating larger temperature ranges it became obvious that some temperature dependency was needed, and an Arrhenius form was assumed for this dependency. The expression obtained for kr is in equation (9):

$$kr = b3 * e^{(-b4)/(R*T)} \quad (9)$$

Equation (1) can b expanded to include a generation term, which is only non zero in the burn room, when HCl is being generated from burning materials. In the GWD study [30], a specific HCl generation function was developed for electrical decomposition of flexible PVC coated onto wire. In other studies, involving burning of rigid PVC, generation functions were developed on the basis of the mass loss rate of PVC (measured) and the chlorine content of the PVC. In some cases HCl was injected directly, in which case the generation function is simply the rate of introduction of HCl into the compartment. Other equations can be developed depending on the scenario and the source of the HCl.

Assessment of the HCl decay model in HAZARD I

The HAZARD I, version 1.1, software was applied to three cases: (a) room-plenum (discussed above), (b) room-corridor-room (also discussed above) and (c) scenario 5, Christmas tree fire, one of the example cases for the HAZARD I method [39].

The Christmas tree fire example involves a townhouse, which has two floors. For HAZARD use, on the lower floor there are two "compartments" (the burn room (8.2 x 4.9 x 2.4 m) and the hall (2.1 x 5.2 x 2.4 m)), a set of stairs (in two more "compartments": a low (1.2 x 2.1 x 2.4 m) and a high (1.2 x 3.0 x 4.9 m) level) and on the higher floor there are two more "compartments" (bedrooms 1 (5.3 x 3.3 x 2.4 m) and 2 (2.9 x 6.1 x 2.4 m)). In reality the house has, of course, several compartments and furniture, but is divided in this way for calculation purposes. The walls and ceilings are painted gypsum board and the floors are concrete (lower floor) and wood (Douglas fir, upper floor). The first item ignited is a natural Christmas tree, which eventually ignites a "bean bag chair" (vinyl covered, with polystyrene foam beads). For this application 454 g of polystyrene beads were replaced by an equal mass of rigid PVC. The generation of HCl was calculated on the basis of a 56% HCl content of the PVC. The HCl generation was based on the assumption that this PVC formulation contained no fillers or other HCl retention catalysts; this is a simplistic approximation. It was assumed, for simplicity, that the replacement of polystyrene by PVC had no effect on heat release or other fire performance.

The key final outcomes of a HAZARD I run are the expected mortality in the fire and the time available for escape. This is accomplished based on one of several tenability criteria, addressing heat, smoke toxicity or a combination of both. The smoke toxicity tenability criterion is based on the N-gas model, which uses a combination of the toxic potencies of various primary toxic gases: carbon monoxide, carbon dioxide, hydrogen cyanide and low oxygen, but does not include HCl, although NIST has already developed a modified formula for the N-gas model which does include HCl [40]. Thus, it is not possible to adequately assess the effect of chlorinated materials on the toxicity of the smoke atmosphere using this criterion. This is an easily solvable problem. There is, unfortunately, an added problem. A further criterion for assessing tenability via smoke toxicity is the use of a generic smoke toxic potency, and the calculation of tenability based on overall mass loss (Ct). This is a very adequate calculation and is, in fact, a better calculation method than the one that is based on individual toxic potencies. However, when HCl is generated, this overestimates smoke toxicity hazard because the tenability is calculated based on mass lost by the fuel burnt and not on the amount of smoke present. The difference between the two is, of course, the amount of HCl that has decayed. This is a problem that is less easily solved, but is a small issue.

Case a: HAZARD I predicts much less HCl decay than is shown by the experimental data. One of the most important reasons for this discrepancy is the fact that the "hot layer" never reaches the floor level in HAZARD I, while it clearly did so in the actual experiment. Thus, HCl decay on a very substantial fraction of the surface (the ceiling tile floor) is ignored. This is made even more important since the rate of HCl decay on ceiling tile is considerably faster than on painted gypsum board. Another concern has to do with the mass flows. This fire involved over 9 m of cable, stretched across the floor, but HAZARD I use a "point source", thereby requiring the smoke (and HCl) to travel much further to any wall surface.

Case b: HAZARD I satisfactorily predicts this scenario, with the caveats that it is essential to subdivide the long corridor into several “virtual compartments” and that a few excessively high values are found early on.

Case c: An analysis was made of the "compartments" in this "packaged" example found in the HAZARD I reference guide. During this analysis it was noticed that the "compartments" are simply one way in which the same floor and ceiling area, and the same compartment height, could be distributed along walls. It was, moreover, observed that other walls present in the house (bathrooms, closets, kitchen furniture) were not used, although they would clearly have served as added sinks for HCl. A simple arithmetical calculation shows that the dimensions of these compartments can easily be changed, within the same house scenario, to achieve higher wall surfaces. Thus, HAZARD I had to be run in an “enhanced decay” mode, where every “compartment” had 50% more walls, but the same floor and ceiling surfaces and the same overall volume. With this change, the HAZARD I model did an excellent job of representing realistic HCl decay data.

OTHER GASES

Hydrogen chloride is not a unique gas when it comes to decay in fires. Other gases with similar characteristics are likely to exhibit similar phenomena in fire atmospheres. Thus, for example, hydrogen bromide (HBr) and hydrogen fluoride (HF), which are the other two common halogen acids found in fire atmospheres can be expected to behave the same way as HCl.

HCl has been studied extensively, with over twenty published papers, to a large extent because HCl is a major product resulting from the combustion of a widely used synthetic material, poly(vinyl chloride) (PVC) [3, 9, 10, 41] which is often present in fires because of its wide range of applications. In fact, the results of two studies, in which fire fighters entered buildings on fire equipped with gas sampling probes, found HCl in one third of the incidents [42-43]. Interestingly, the highest HCl concentration measured in either of these studies was only 280 ppm [44], in spite of typical emissions of HCl from PVC (and other materials) that can be in the region of thousands of ppm. Therefore, studies of fire hazard need to take into account HCl decay in order to avoid overestimating the fire hazard of materials containing PVC. HCl can also be generated from the combustion of materials containing chlorinated fire retardants or from the combustion of other chlorinated polymers or even from reactions involving common chlorinated salts. It is not uncommon to have any of these phenomena occur.

HF is generated from the combustion of fluorinated polymers, which are also very common in the built environment. HBr is generated from the combustion of polymers that have been fire retarded with brominated materials, or that contain some brominated sections in the backbone. It is rare to have high volumes of inherently brominated polymers or of polymers containing high levels of fluorinated additives (as fire retardants or in other roles). Both HF and HBr are strong acids, similar in that respect to HCl. It can be assumed that the rate of decay of HF and of HBr in fires will be similar to that of HCl. Unfortunately no studies have been published that have looked into this issue, and that is why the present work has focused primarily on HCl.

Another common gas found in fire atmospheres and which has key toxicological importance is hydrogen cyanide. It is, at best, a very weak acid with limited reactivity to the type of construction surfaces that are common in the built environment. A few years ago, a study looked into the yields of several combustion products in large scale fires, including HCl, HCN and carbon monoxide [45], but some experimental difficulties in the study have meant that it is difficult to rely quantitatively on the data obtained [46]. Earlier, another NIST study in 1991 was able to measure some HCN concentrations in real scale fires and they found some differences with small scale yields [47]. Unfortunately, while the 1991 NIST study clearly showed that HCl decayed it was less clear about HCN decay. In summary, it is not possible at present to assess the importance of decay to the toxic hazard from HCN in fires.

CONCLUSIONS

It is worth noticing that there is significant amount of information [48-50] that indicates that the smoke toxicity from most materials is within a very narrow margin (see Figure 7) and carbon monoxide is the overwhelmingly important toxicant in fires, especially those that go to flashover.

With regard to acid gases (and particularly hydrogen chloride) there is no longer debate possible: the concentrations of HCl that can be found in fires in real buildings are much smaller than would have been predicted from an analysis of the chlorine content of the "fuel". This is an essential consideration for toxic hazard since the concentrations of other combustion gases, such as carbon monoxide, decrease only by physical entrainment and dilution processes. Thus, the relative toxic importance of HCl, as compared to carbon monoxide, decreases as the smoke layer moves away from the fire zone.

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GLOSSARY

d[HCl]/dt:	rate of change of HCl atmospheric concentration, in kg/(m^3 s).
[HCl]:	concentration of HCl in the gas phase, in kg/m^3.
$[HCl]_i$:	concentration of HCl at the interface, in kg/m^3.
kc:	convective mass transfer coefficient; in m/s.
$[HCl]_w$:	concentration of HCl on the wall, in kg/m^2.
Ke:	HCl partition (or gas/wall equilibrium), coefficient, in m.
kr:	HCl decay rate coefficient inside the surface, in 1/s.
F1:	term denoting partition coefficient dependency on [HCl] and temperature; it represents adsorptivity of the surface for HCl in absence of water, in 1/m.
F2:	term denoting partition coefficient dependency on water concentration; it represents added capacity for HCl adsorption as a function of the water present in the gas; dimensionless function.
V:	gas volume of compartment, in m^3.
A:	surface area where decay takes place, in m^2.
$[H_2O]$:	concentration of water, in kg/m^3.
$[H_2O]_s$:	saturation concentration of water, also in kg/m^3.
b1:	fitted surface parameter, representing the temperature dependency, in m.
b2:	fitted surface parameter, also representing temperature dependency, but expressed in m^3/kg.
b3:	fitted surface parameter, representing the first order reaction pre-exponential factor, in 1/s.
b4:	fitted surface parameter, representing the activation energy, in J/g mol.
b5:	fitted surface parameter, representing dependency on humidity, in units of $(m^3/kg)^{b7-b6}$.
b6:	fitted surface parameter, also representing dependency on humidity; it is dimensionless.
b7:	fitted surface parameter, also representing dependency on humidity; it is dimensionless.
T:	temperature, in K.
R:	ideal gas constant, 8.314 J K^{-1} mol^{-1}.

Figure 1 - Effect of repeated surface exposure on HCl decay

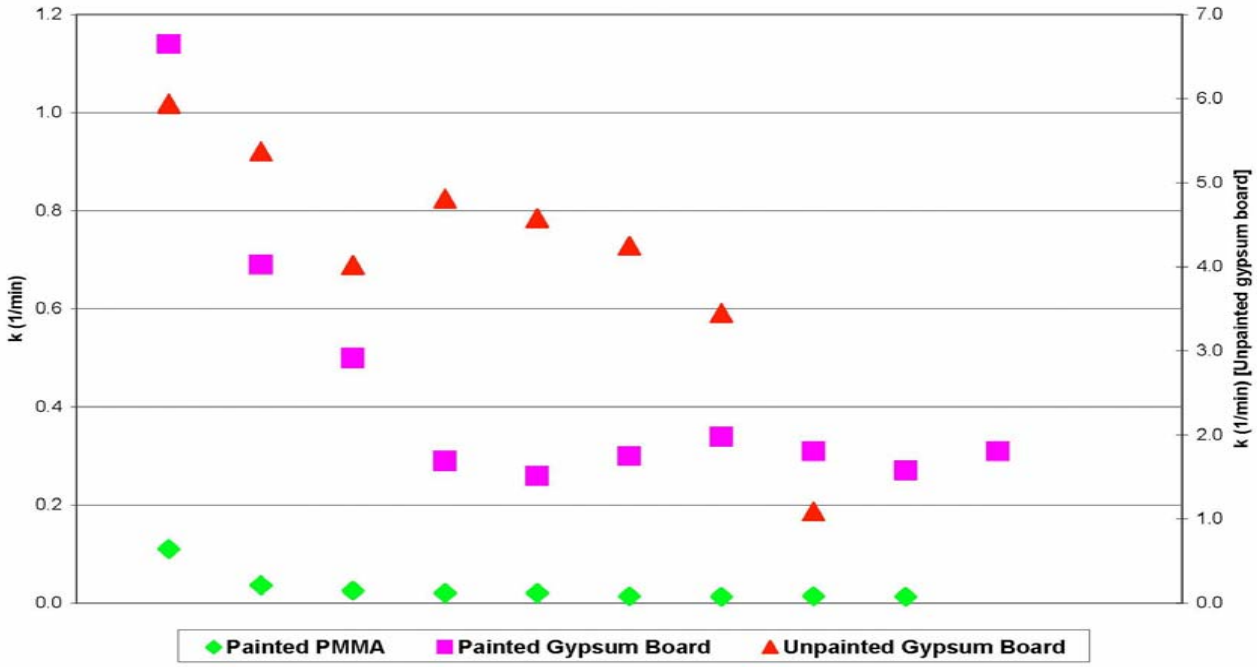


Figure 2 - Effect of humidity on HCl decay on painted gypsum board

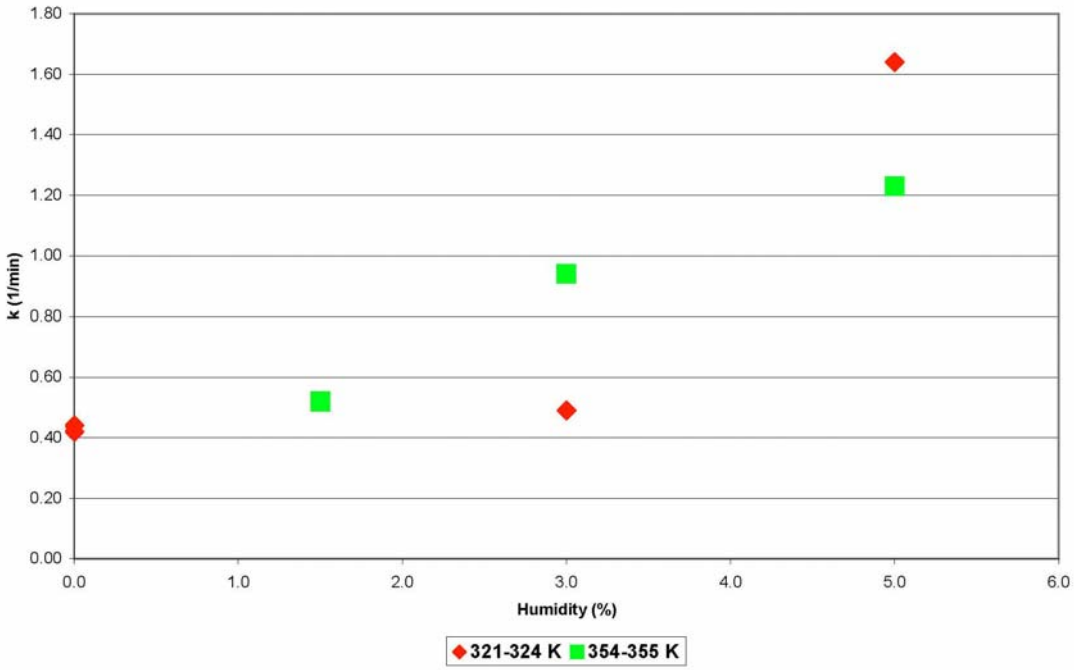
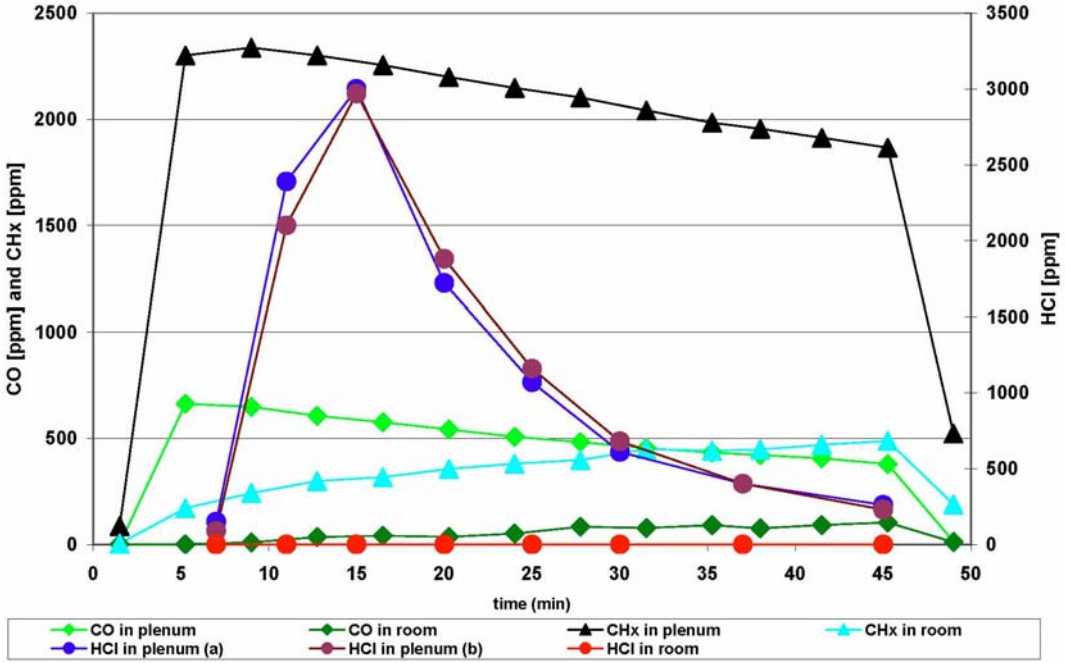


Figure 3: Concentrations of HCl, CO & CHx in Plenum and Room



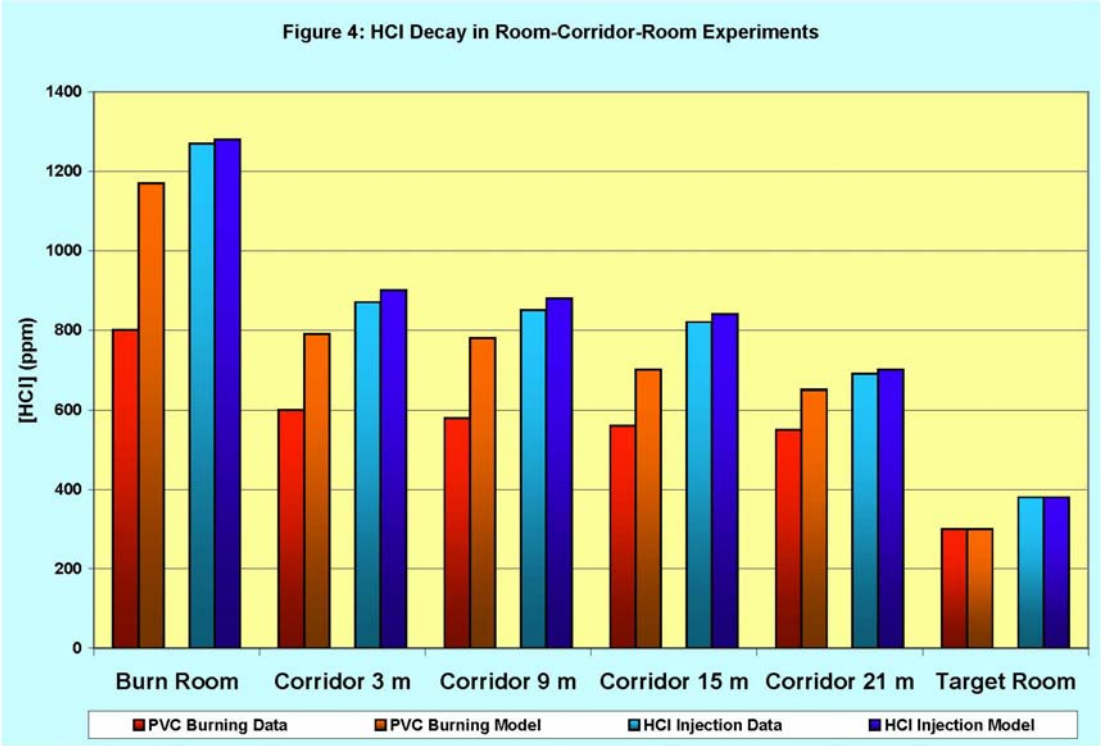


Figure 4: HCl Decay in Room-Corridor-Room Experiments
[HCl] (ppm)
1400
1200
1000
800
600
400
200
0
Burn Room
Corridor 3 m
Corridor 9 m
Corridor 15 m
Corridor 21 m
Target Room
PVC Burning Data
PVC Burning Model
HCl Injection Data
HCl Injection Model

Figure 5: HCl decay in HVAC runs with gypsum board

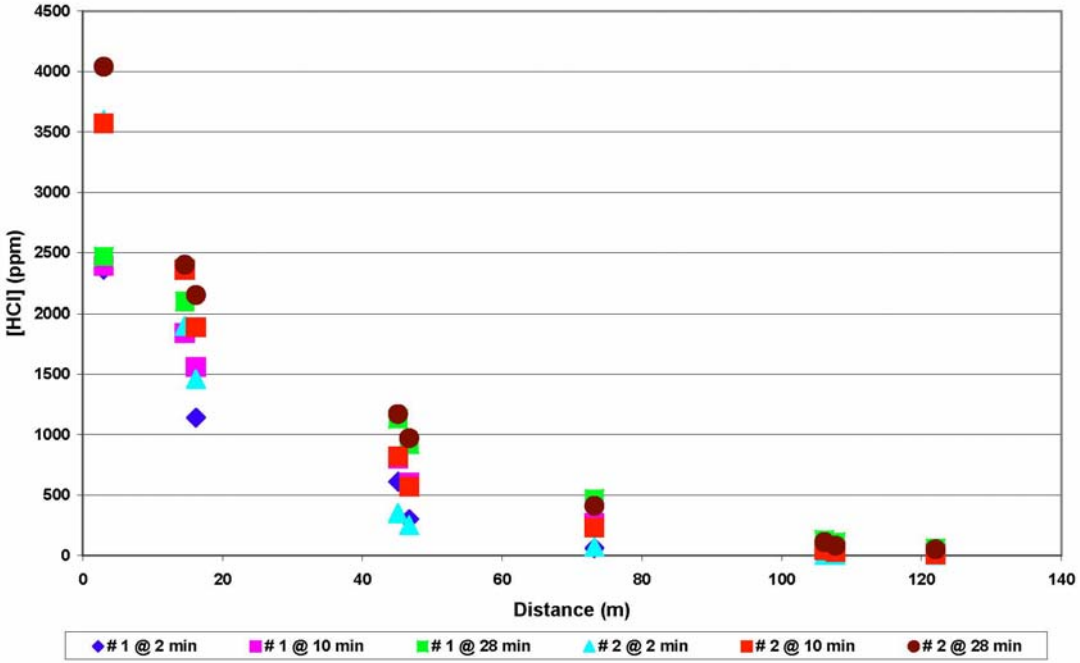


Figure 6: HCl decay in HVAC tests with PMMA

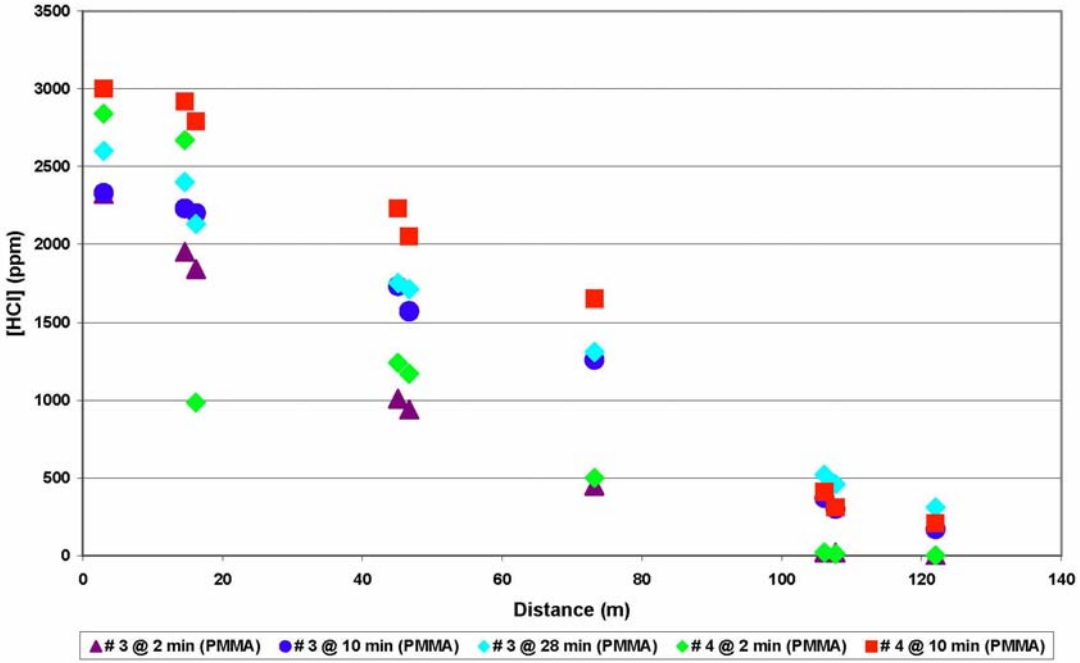
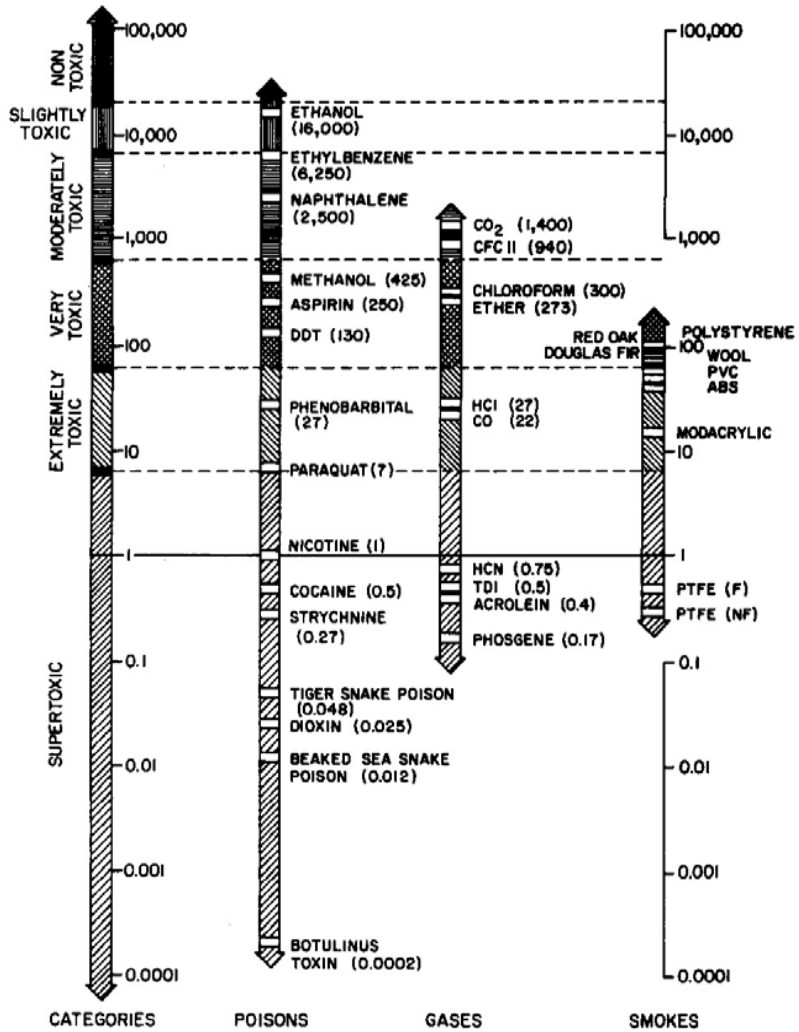



Figure 7: Ranges of smoke toxic potency of polymeric materials and other gases