A NEW FRONTIER FOR CONTAMINATION: REACHING THE MOLECULES

J-F. Roussel(1), D. Faye(2), M. Van Eesbeek(3), T. Tondu(1), R. Migliore(2), R. Rampini(3), T. Paulmier(1)

(1)ONERA-DESP, 31055 Toulouse, France, Email: Jean-Francois.Roussel@onera.fr
(2)CNES-CST, 31401 Toulouse, France, Email: Delphine.Faye@cnes.fr
(3)ESA-ESTEC, 2200 AG Noordwijk ZH, The Netherlands, Email: Marc.Van.Eesbeek@esa.int

ABSTRACT

This papers starts with a review of the contamination physics and of the most widespread engineering approaches to contamination assessment. Then the main questions still open to validate the European physical approach are discussed. Emphasis is set on the important point of a realistic separation of chemical species, probably a prerequisite for a physical modelling. Several original results are presented. Some lead to a quite clear conclusion, like the pre-eminence of the limitation by desorption over the limitation by diffusion for outgassing. This observed trend needs yet to be validated on other materials.

1. INTRODUCTION

In the last ten years many contamination studies were performed in collaboration between CNES, ESA and ONERA. A first important topic was the improvement of the physical approach to contamination as used in Europe since 1985 [1], the subject of this paper. The second major topic was contamination-photon synergy, and it is reported elsewhere including in this conference [2, 3].

The physical approach to contamination is in principle very powerful since it can address all situations in flight, as e.g. thermal cycling and variable temperatures, inducing re-emission. The involved physical phenomena are however complex, and a detail modelling of all of them is clearly impossible. Keeping presently in mind that our final objective is contamination engineering and not science, our main guideline in this quest of a physical understanding of contamination processes must be to assess the relative importance of phenomena in the typical situations of interest, in term of materials, temperatures, etc. Then, the simplified physical view and simplified physical model we will develop might prove useful for the engineer.

The contamination engineer needs to assess contamination deposits and their effects on various subsystems or functional materials. Very important, he must do that at mission time scale for realistic conditions (e.g. with thermal cycling). The capability to extrapolate data obtained on ground during short experiments over years in flight is thus of the first importance.

This capability of extrapolating at very long times is a priori an important asset of a physical model, if successful. The alternative approach, consisting in a direct empirical extrapolation must yet be considered carefully. If the more complex physical approach does not supply better extrapolations, it can somewhat be considered a failure. This is another reason for doing our best effort to improve and validate it (or them).

This paper starts by reviewing contamination physics, needed to understand the following steps. Next, we review the two approaches, the empirical and the physical one as they are used today. This is another prerequisite to a more detailed physical analysis. In the next section we discuss most questions still open in the physical approach. In a last section we discuss the major improvement idea, which would solve the weakest point of this approach, i.e. performing a realistic separation of the outgassed species. A good physical model can probably not be obtained before this new frontier is reached.

2. REVIEW OF PHYSICS

Contamination physics can be split in three steps, the emission of contaminants, their transport, and finally the physics of the deposit.

The diversity of possible contaminant sources is large (outgassing, thrusters, vents, dumps, material erosion…), but we will focus here on the often dominant source, i.e. outgassing.

Material outgassing itself can be seen as consisting of two successive steps. Contaminant molecules embedded within the bulk material, such as e.g. polymerisation residues, must first diffuse to the surface (Fig. 1). This can usually be described by Fick's law for the flux f and volume density n_{vol}

$$f = D \ dn_{\mathrm{vol}}/dx$$

with a temperature activated kinetic constant D.

Emission to vacuum is then conditioned by desorption. The desorption flux is assumed to be a first order law with respect to the surface density

$$f = k \ dn_{\mathrm{surf}}/dx, \ k = 1/\tau \ ,$$

the kinetic constant k being the inverse of a time constant, follows an Arrhenius law.

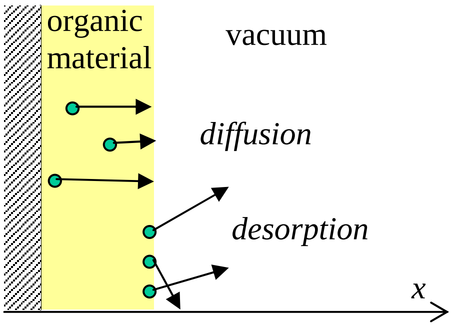

Fig. 1. Outgassing: diffusion followed by desorption

What we usually call transport is:

- Line of sight (direct view transport)
- Reflections on surfaces
- Gas phase collisions

The physics involved in this field is globally known, although this is not necessary true for all cross sections or reflection distribution functions; We will however not discuss it further here.

We will focus more on the physics of the deposit. The condensation of impinging molecules is usually supposed to be total, although immediate bouncing is possible (in particular for supra thermal velocities). Since the layer of deposited contaminants is thought to be thicker than the one on the top surface of an outgassing material, its emission law is likely to differ from the first order law above describing desorption. A thick deposit rather follows an evaporation law with a flow rate independent of its thickness (zero-order law), which can be related to its vapour pressure through Langmuir law

$$\frac{dm_{\mathrm{evap}}}{dt} = -0.044\sqrt{\frac{M}{T}}\,P_s(T)$$

for a pure contaminant (more on mixing in section 4).

A first complexity step stems from surface tension effects. Above some thickness, and depending of the molecule affinity with the substrate, thin films may tend to gather in clusters or droplets (see example on Fig. 1). Of course this may change the evaporation rates by orders of magnitudes. It is today extremely difficult to predict the formation of such clusters, in particular in the case of a contaminant mixture (reality!) and of possible extra interactions such as photochemistry. Mixing effects can also complicate the picture.

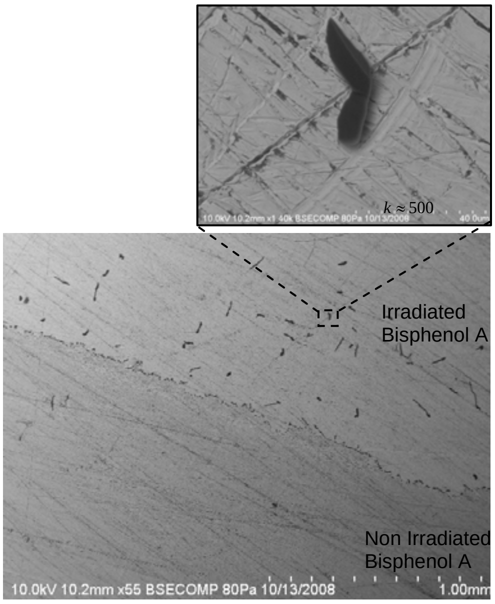

Fig. 2. Bisphenol A deposited as a film (lower part) or creating clusters (upper part), as a results of UV irradiation in this case.

Chemistry is another huge source of complexity in the deposit, which we only summarise briefly here. UV photons can generate radicals (or ionisation), initiating radical reactions finally leading to reticulation, photolysis, chromophore creation… Another paper presented at this ISMSE [2] deals with recent advances in this field. Another radical at the origin of such reaction is the ambient oxygen atoms. At first order it is usually considered as leading to the oxidisation of silicones into silicates (permanent deposit) and the erosion of other organic contaminant as confirmed by flight observations [4].

The detrimental effects of such deposits are essentially related to interactions with light. The most important is in most of the cases related to an increase of sunlight absorption by the generated chromophores or colour centres. These can impact thermal control, optical systems, solar cell power, etc. A change of infrared emissivity can also impact thermal control. Light diffusion can also become important, in particular in case of cluster formation.

3. DIFFERENT APPROACHES TO CONTAMINATION

The overall contamination processes described in previous section appears as overwhelmingly complex. Space system engineers must yet produce contamination assessments too as guidelines to design and for qualification. The experimental approach is usually limited to material testing. A refined analysis at system level is usually intractable and modelling is the preferred approach. The main difficulties are the complexity of the involved phenomena and the need to extrapolate necessarily short experiments to years long space missions.

In this perspective several simplified approaches were developed. The first approach described is essentially empirical, while the second tries to model the most important physical phenomena through a series of simplified laws.

3.1 The empirical approach

The major attempt to address contamination assessment by a direct empirical approach is the ASTM 1559 standard [5]. Very briefly, this well known method consists in measuring on QCMs (Quartz Crystal Microbalances) the deposition of contaminants originating from a sample material in an effusion cell (see Fig. 3). The temperatures of the outgassing material and of the QCMs are maintained constant over a few days and a set of different temperatures is tested for both. A TGA (Thermogravimetric Analysis) is usually performed at the end of the test to obtain information on the volatility of the contaminants.

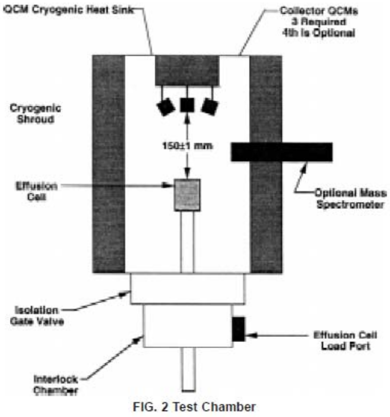

Fig. 3. A typical experimental setup for dynamical characterization of outgassing and condensation, from [5]

Based on these data, the practical assessment method for a space missions is usually the following. Worst case temperatures are selected in the datasets with respect to flight data (upper temperature for the source and colder for the deposition surface). The corresponding experimental data (extending over a few days) are then mathematically extrapolated (to many years missions), through some power law or logarithmic law.

The pros of this method are its simplicity and directness. On the other hand it is limited (e.g. no heating-based re-emission can be modelled) and there is no physical justification of mathematical extrapolation at mission time scale.

As an illustration of the latter difficulty, we made a fit of a four day constant temperature CVCM (Collected Volatile Condensable Mass) by four laws (two power laws, two logarithms), which is displayed in Fig. 4. It is never possible to accurately fit such data by a single law over the whole period since the beginning is quite different. Hence we focussed more on the fit of the last two or three days.

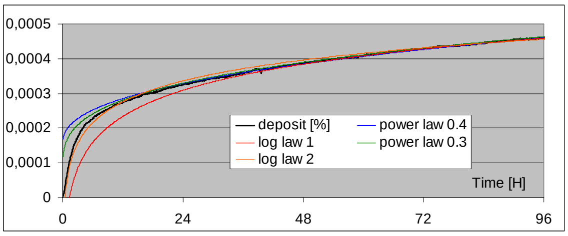

Fig. 4. Fit of an experimental EC2216 deposit at constant temperature (CNES data) by four different laws.

We next played the game of extrapolating these fits to typical mission duration (see Fig. 5). Clearly the arbitrary choice of the fitting function can yield discrepancies close to a factor of five in this example. Logarithmic laws are more optimistic, while power laws are more conservative.

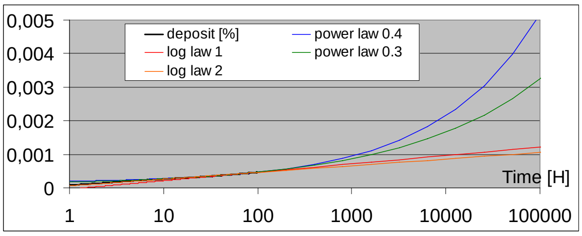

Fig. 5. Extrapolation of the four previous fits to mission time scale (100000 H = 11 years)

3.2 The physical approach

Since 1985 Europe developed a more physical approach [1]. The complex emission physics was simplified into a residence time approach (1^{st} order law, representative of desorption), both for outgassing and re-emission.

$$\frac{dm^{\alpha}}{dt} = -\frac{m^{\alpha}}{\tau^{\alpha}(T)}$$

where m_{α} is the available mass of contaminant α, and τ_{α} its residence time. The residence times are supposed to follow an Arrhenius law

$$\tau^{\alpha}(T) = \tau_0^{\alpha} e^{E_A^{\alpha}/RT}$$

usually linearised (in the exponential) to simplify computer treatment in the eighties:

$$\tau^{\alpha}(T) = \tau_0^{\alpha} e^{-k^{\alpha}(T-T_0)}$$

The total contaminant mass (remaining in the outgassing material, or deposited all over the spacecraft after transport computation) is then obtained as the sum of masses of all contaminant species α.

This approach supplies temperature dependences. It allows thus physical extrapolation to any temperature profiles, and also to long term durations since a ground experiment at high temperature can be viewed as an accelerated experiment. Typical test procedures involve increasing temperature steps (Fig. 6). The acceleration at the steps allows extracting the acceleration factors of the Arrhenius-like laws for time constants. It can be mentioned that the COMOVA code is based on this approach [6].

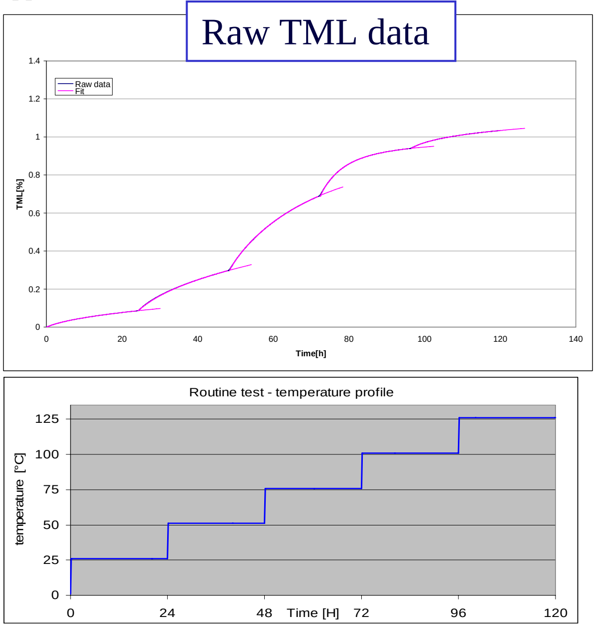

Fig. 6. Example of TML (Total Mass Loss) on the upper panel, with the classical stepwise temperature profile on the lower panel (ESTEC data)

Then a long term extrapolation can be performed, including the extrapolation at constant temperature displayed in Fig. 7. Extrapolation towards too large temperatures is of course not possible since it would require experiments at higher temperatures than available.

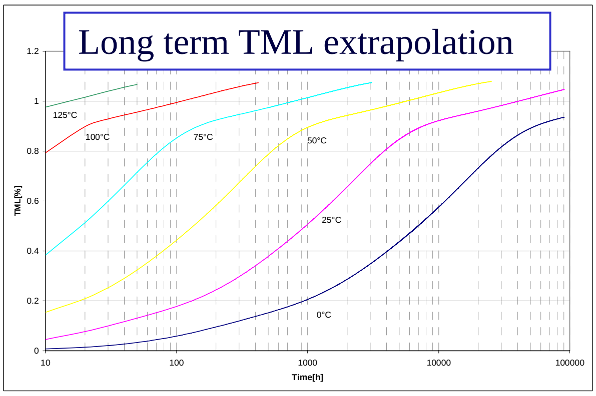

Fig. 7. Constant temperature long term extrapolation from the data above and the physical residence time approach.

This is an ambitious and difficult approach. It is more powerful (variable temperature, re-emission modelled) and in principle more representative of reality than the empirical approach. It is however not yet fully clear whether this simplified physical modelling is close enough to real physics to lead to better predictions. The extraction of the numerous parameters is another difficulty that impacts the global assessment process. In particular in the absence of chemical information (through e.g. mass spectrometry.) the separation of species (attributing the total mass emitted by the sample or deposited on the QCMs to different chemical species, even chemically undetermined) is particularly approximate.

The key point in such a necessarily simplified physical approach is certainly to capture (model) the important part of the physics and discard the superfluous part. We discuss the simplifications and assumptions of this approach in next section.

4. Open questions / Difficulties

4.1 Diffusion versus desorption

The first open question concerning outgassing is the relative importance of diffusion and desorption in usual materials. Of course both phenomena exist and limit the outgassing rates, but for a simplified approach it is crucial to determine whether outgassing is mostly diffusion limited or desorption limited.

Although the current modelling assumes a desorption limited outgassing, some elements point at a possible importance of its limitation by diffusion. For example, Fig. 8 shows that toluene can be detected over four successive temperature steps, from 50 to 125°C. However modelling outgassing by desorption usually leads to species being completely emitted faster, over two or three temperature steps.

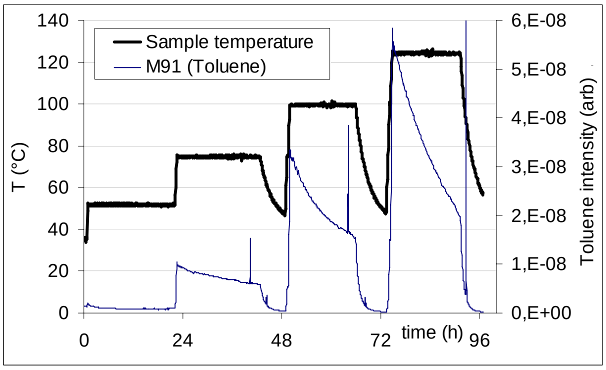

Fig. 8. Toluene emission rate from EC2216 (based on mass 91 measurement by mass spectrometry) during four temperature steps (50, 75, 100 and 125°C)

This is why we tried to determine whether experimental data were more consistent with a limitation by diffusion or desorption. A first attempt consisted in modelling an experiment with either assumption and comparing with the data. This approach was however not very successful (no clear discrimination between both assumptions) probably because, on the basis of total deposit measurements, we were unable to correctly separate species.

A second approach proved more successful. It stayed at the level of the total deposit, with no need to perform a correct species separation. The idea was to consider how outgassing rate should scale, when we vary the diffusion length (or effective material thickness) of a material depending on the assumption done. We used a reference material, either as a thin layer of glue deposited on aluminium, or the same layer of glue sandwiched between two foils of aluminium (Fig. 9). In the 2D view of the figure, the diffusion length *L* of the sandwiched sample is no longer its width but its half extension. In 3D we generalised the definition of the diffusion length as the ratio of the sample volume to its exposed surface.

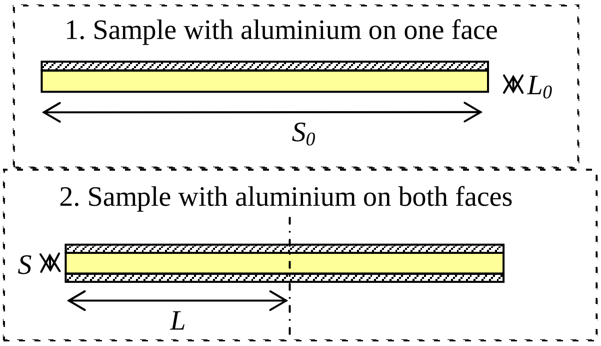

Fig. 9. Exposed surface *S* and effective diffusion length *L* of a reference sample (aluminum on one side) and a sandwiched sample.

Then we studied how the outgassing rate should change when going from small L_0 to large *L* diffusion length. In the extreme case of a pure limitation by diffusion, desorption is immediate (hence a quasi zero density at the surface sample, upper part of Fig. 10) and inefficient diffusion does not allow deep contaminants to reach the surface. In the other extreme situation, diffusion is very efficient, hence the flat densities in the lower part of Fig. 10, and outgassing is mostly limited (i.e. controlled) by surface desorption). In this second case the material behaves like a contaminant tank.

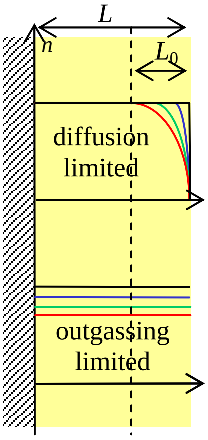

Fig. 10. Extreme cases of limitation by diffusion only (upper panel) or desorption only (lower panel). The color density profiles correspond to successive levels with time (initial one in black).

Working with relative contaminant mass emissions ΔW, normalised by the sample mass

$$\Delta W \equiv \frac{\Delta m_{\text{contaminant}}}{m_{\text{sample}}}$$

we next examined how ΔW for the sandwiched sample could be obtained from for the reference sample mass loss ΔW_0. In the case of the pure diffusion limitation, this is very easy. Assuming that diffusion is not effective much deeper than L_0, the outgassed mass is simply proportional to the exposed sample surface *S*, regardless of its effective thickness *L*, which simply gives for the relative masses a scaling with the thickness:

$$\Delta W(t) = \Delta W_0(t)\frac{L_0}{L}$$

Time derivation yields the same scaling law for the mass loss rate:

$$\Delta \dot{W}(t) = \Delta \dot{W}_0(t)\frac{L_0}{L}$$

Not surprisingly both the emitted mass and its flow rate are simply reduced by the thickness ratio.

In the inverse situation of a limitation by desorption, the differential equation ruling outgassing (emission flow rate proportional to the surface density) must be studied to see that the thickness change results in a time scaling for the mass emission:

$$\Delta W(t) = \Delta W_0\left(t\frac{L_0}{L}\right)$$

This is not surprising since a thicker material is simply a bigger tank with the same "leaking" flow (as a function of the tank relative level). In this case, time derivation yields an extra factor:

$$\Delta\dot{W}(t) = \frac{L_0}{L}\Delta\dot{W}_0\left(t\frac{L_0}{L}\right)$$

For this relative masses, the mass emission ΔW is delayed, while its flow rate $\Delta\dot{W}$ is both delayed and scaled down so that its time integral be unchanged.

Since these scaling laws are significantly different we expected a very conclusive comparison with experimental data. The next two figures (Fig.11 and Fig. 12) display experimental mass flow rates for small and large diffusion lengths, and theoretical scaling of the reference case data to conditions of the sandwiched one. We have used CNES and ESTEC data, TML and CVCM.

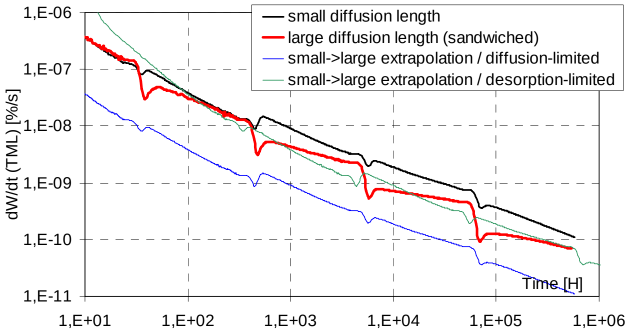

Fig. 11. Experimental TML rate (RTV S691, ESTEC data) of: a reference thin layer (black), a sandwiched layer (red), to be compared to the former scaled according to diffusion limitation law (blue) or desorption limitation law (green). The five temperature-accelerated 24H steps were transformed into an equivalent constant temperature 25°C long time series.

The conclusion is very clear. In both cases the matching is much better, and quite good, in the assumption of a desorption limited outgassing. This is a very interesting result. We are forced to conclude that, in spite of the possible importance of the limitation by diffusion in some situations (for very large sandwiched materials, but ours were already a few centimetres), general situations are much more controlled by desorption.

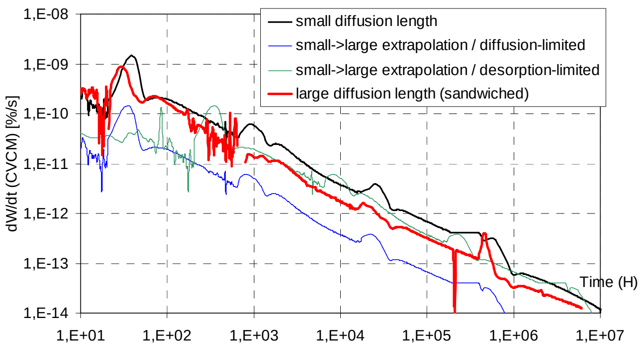

Fig. 12. Experimental CVCM rate (EC2216, CNES data) of: a reference thin layer (black), a sandwiched layer (red), to be compared to the former scaled according to diffusion limitation law (blue) or desorption limitation law (green). The initial part is a noisy because of a small CVCM.

This is a rather robust result. The reason is that an important limitation by diffusion would unavoidably lead to an L_0/L scaling of the mass flow rate. And comparison of the scaled reference data to the sandwiched data is absolutely direct (in particular not dependent of the heating-acceleration we applied to the time axis of the two figures above). The possibilities for an important role of diffusion limitation can probably only be found in special cases: very long diffusion lengths, maybe some species that were minor in our data (very heavy ones?), some specific materials…

4.2 <u>Order 1 law versus order 0 law</u>

Another open point concerning contaminant emission is whether it should be described by a first order desorption law or a zero-order evaporation law. This question mostly arises for the re-emission of deposited contaminants, since primary outgassing of a material is not thought to lead to thick surface layers (unless contaminant-material affinity is unlikely small).

This question may not deserve very long discussions since reasonable assumptions allow modelling simultaneously both regimes and the transition in between. Assuming a BET-like [7] structure of the deposit layers (resulting from a condensation-re-emission equilibrium), and neglecting the difference of affinity between molecules themselves and with the substrate (only because getting such data would be too much work in practice) the following total emission rate can be derived (by summation over layers) for a pure contaminant:

$$\left(\frac{dm}{dt}\right)_{\text{re-emission}} = -\frac{m}{\tau_{\text{re-em}}(T)}\cdot\frac{1}{1+\frac{m}{m_0}}$$

The m_0 constant is the mass of a monolayer. Assuming an ideal solution (same affinity between molecules α and β as between α themselves, and efficient enough diffusion) we also derive

$$\left(\frac{dm^{\alpha}}{dt}\right)_{\text{re-emission}} = -\frac{m^{\alpha}}{\tau^{\alpha}_{\text{re-em}}(T)}\cdot\frac{1}{1+\frac{m_{tot}}{m_0}}$$

where m_{tot} is the total contaminant mass. It can be checked that this formula asymptotically gives all the previous ones in case of submonolayer deposit (first order law), thick deposit (zero-order law) or a single contaminant (law above). It is also consistent with Raoult's law for ideal solutions. We start using it in our new modeling activities.

4.3 Other deposit physics

However these assumptions are not always valid. Without considering chemical reactions that are outside the scope of this paper, it is true that the assumptions of the last subsection are not always fulfilled. Although we can offer few answers to the questions raised we chose to quickly review these effects.

First the surface affinity issue (which can be generalised to both surfaces of a layer, i.e. to its vacuum interface) lead to the formation of clusters or droplets mentioned in section 2. This is not an uncommon experimental observation. Its consequences on the emission rates can be very large as can be seen in Fig. 13. The shift a few tens of degrees in the displayed TGA are the consequence of an emission rate different by more than one order of magnitude.

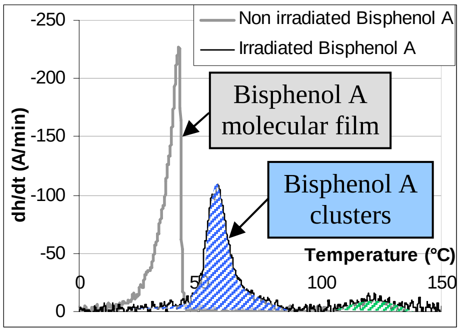

Fig. 13. Emission rate from a film or a clusters of bisphenol A during a TGA

Although some modelling of droplet evaporation can be done, the formation of the droplet is too difficult to predict and we are not aware of any practical progress in this direction. Their formation depends on the surface affinity, the contaminant mixture, and also seems to be quite sensitive to UV (with both effects observed, blocking or formation of clusters under UV).

Similarly, non ideal mixture effects (different affinity between homogeneous and heterogeneous molecules) are certainly too difficult to assess for any practical usage. There too many different (unknown) molecules.

A different effect that leads to a violation of the ideal solution assumption is the blocking of diffusion within the deposit (no mixture at all!). The successive or simultaneous deposition of water, methanol or toluene on a cold sample were shown [8] to have important consequence on their re-emission rate, through the formation of layers. It is not clear to us whether such situations are exceptional or could arise in our applications. In this case of a frozen deposit another way of obtaining layer effects could be the selective evaporation of a given compound within the top layers (sublimation).

Let anticipate a little and mention that the results displayed in section 6, focussing on species separation, also show the absence of mixing effects in that case.

4.4 Test procedure

From an engineering context, developing a representative physical model is not enough. We must also be able to extract the needed parameters through experiments, both efficiently and accurately enough.

A first major difficulty is species separation. Since modelling is made on a per species basis, experiments should supply a method to determine each species quantity. However the current test procedure only gives total deposits, which are difficult to split into each species contribution. This very important topic, central to this paper, is treated in section 5.

Here we shall only treat another experiment-related topic, the equivalence of cold and hot chamber experiments. The simplest and most common approach is using a cold chamber (or shroud). The transport is straightforward (see Fig. 14) and view factors can easily be computed (and of course measured).

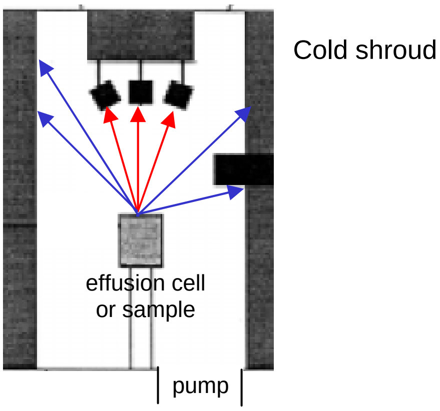

Fig. 14. Principle of a cold chamber experiment: red trajectories contribute to QCM deposit, blue ones do not (all are direct line of sight).

If the chamber walls are hot (at least as much as the effusion cell) transport is very different (see Fig. 15). The fraction of contaminants that reach the QCMs is different but it can also be computed, leading to effective view factors. If the pump orifice is small enough and no long condensation happens on the hot walls (in principle valid for walls warmer than effusion cell), all species gas phase distribution become homogeneous and isotropic. Their mass flow rates to QCMs and to the pump are then proportionnal to the relative areas of these sinks. A small complication arises yet when some QCM's at intermediate temperature are not a sink for all species. This effect remains negligible if the QCM areas are small compared to the pump orifice area.

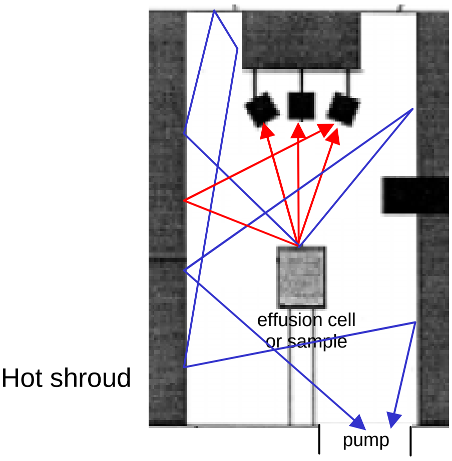

Fig. 15. Principle of a hot chamber experiment: red trajectories contribute to QCM deposit, blue ones do not (the only sinks are the QCMs and the pump, other reflections simply contribute to thermalisation and homogenization).

4.5 Validation

Whatever the approach, empirical or physical, the extrapolation to flight conditions, and moreover to mission duration, must be validated. The idea consists in performing the regular test procedure and predicting another case on this basis. For the empirical approach, the other case should be a (much) longer test, while it can be any temperature profile in the physical approach, which claims to model any profile. We essentially have in mind outgassing and condensation here, leaving aside the more difficult topic of re-emission and deposit physics.

We started working in this direction following the European physical approach. We defined four non standard temperature profiles for validation (see Fig. 16 with three ramps and a constant temperature profile).

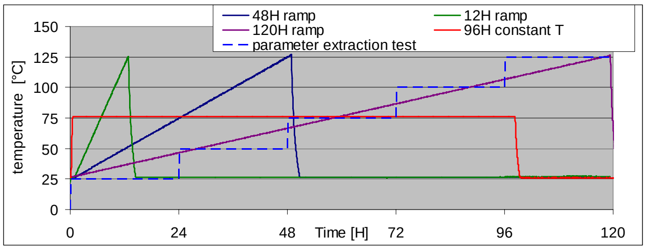

Fig. 16. Different temperature profiles for the effusion cell: the regular 5 steps routine test for reference and four validation tests: three ramps and a constant temperature 4 day long test.

For reference we give the modelling of a TML and CVCM of regular five step test in Fig. 17. The outgassing model is the one described above, while CVCMs are obtained from temperature dependent sticking coefficients used in COMOVA [6]. All parameters of the model are tuned so as to obtain the best fit of the data. For each of the six species α we have: initial mass $m^{\alpha}{}_0$, its residence time $\tau^{\alpha}{}_0$, its temperature dependence coefficient k^{α} and two parameters describing the $S(T)$ sticking coefficient [6] (re-emission matters little here).

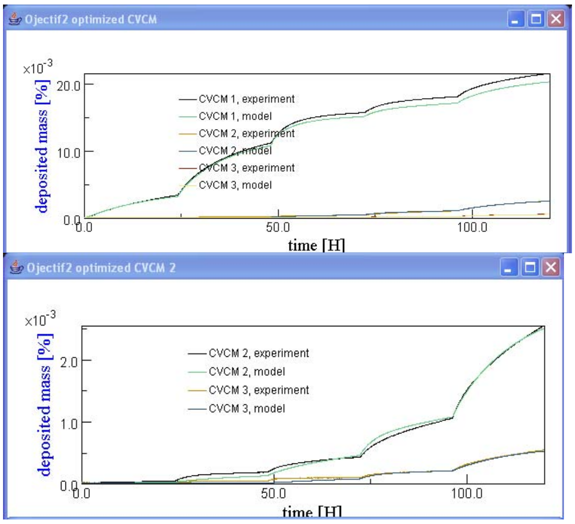

Fig. 17. Fit by the physical model of a TML and three CVCMs (EC2216, regular 5 steps of Fig. 16, CNES data, ONERA model).

Then we modelled the four validation tests with the parameters that were optimised for the regular test. The comparison with the experimental data is given in Fig. 18. The trend is generally good, but the quantitative agreement is not very good, with a few tens of percent of discrepancy. It would be important to know how this error behaves in the longer term. The error is not especially larger on the longer tests.

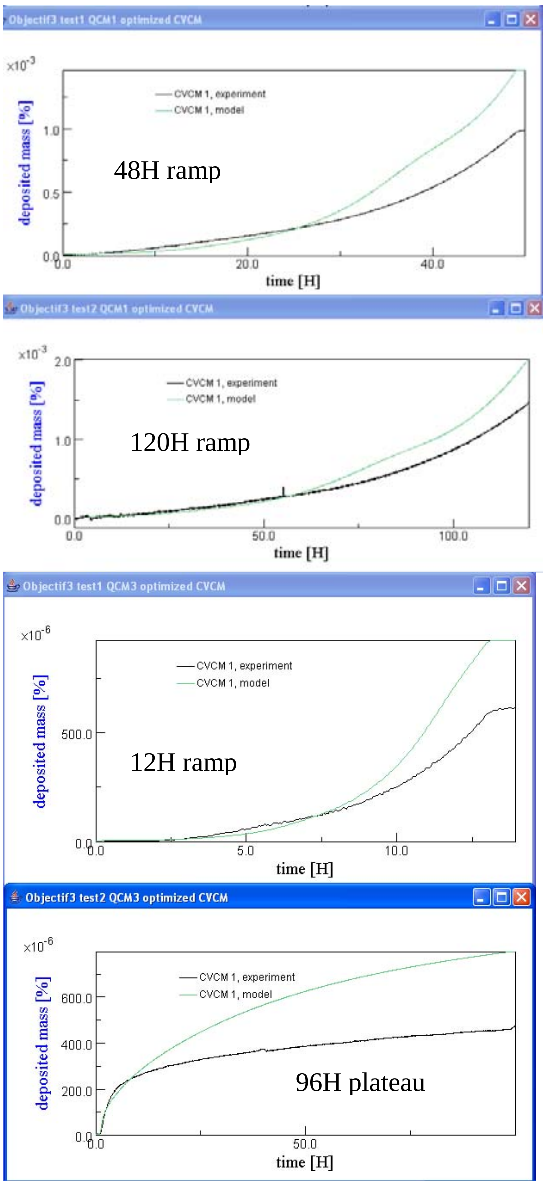

Fig. 18. The four validation tests (temperature profiles of Fig. 16): experiment and model with parameters determined from the standard test

5. SPECIES SEPARATION, A PREREQUISITE TO A PHYSICAL MODELING?

We mentioned species separation as one of the weakest points of the physical approach as it is used today, i.e. only on the basis of global TML and CVCM measurements. If the species separation in the model is not representative of reality, the model can be viewed as a fit by a mathematical sum of functions ("stepwise accelerated exponentials" for first order law).

We considered two main improvements of the tests. Since global deposits do not supply any direct information on the species, we had to go to different measurement. The first idea consists in performing TGAs of the deposit (already in ASTM E 1559). Although limited to a global mass measurement, progressive heating of a QCM results in some species separation. The separation, made on physical grounds, will not distinguish different chemical species of similar physical properties (residence time). It might yet be sufficient for our purposes.

The second possible improvement is the usage of a mass spectrometer or RGA (residual Gas Analyser), necessarily in conjunction with some separation technique (otherwise mass spectra of too many species combine and make interpretation impossible). Less accurate than gas chromatography, but much easier to implement, in particular in situ, thermogravimetric analysis was used to perform some species separation. It might not become part of the routine test procedure we want to define, but proves at least very useful at R&T level.

As a first example Fig. 19 display the mass flow rate evaporating from a QCM during a TGA. The presence of overlapping peaks indicates some species separation, albeit imperfect. This is typical (see e.g. [9] for an application of TGA to contamination UV synergy characterization).

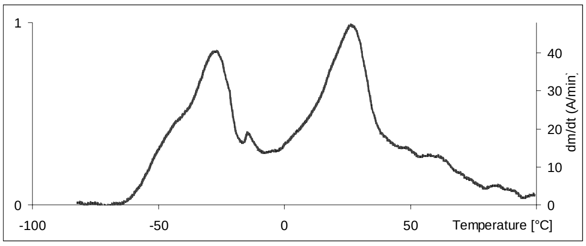

Fig. 19. Example of TGA (2K/min) of a contaminant deposit originating from EC2216 (ONERA data).

Using also an RGA allows a better interpretation. Six masses are displayed on Fig. 20. Masses 109 and 125 seem representative of two different chemical species, showing that the second peak is probably due to at least two species. Its slow decrease is also probably due to several species (cf. masses 36 and 212). The first peak is also at least double (cf. masses 47 and 94). It is thus clear that MS measurements are an important improvement to TGA. The extra effort needed (measurement and data processing) is however also important. It is thus not clear today whether mass spectrometry should be part of new routine tests in the future.

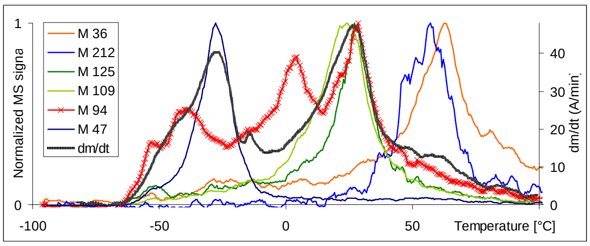

Fig. 20. The same TGA with six concomitant mass measurements by mass spectrometry.

We also performed TGAs from deposits collected on QCMs at different temperatures (from similar fluxes). If we group in the same graph the TGAs from QCMs that were maintained at 0, -25, -50 and -75° during the deposition phase, very interesting features appear (Fig. 21).

First, TGAs are very similar at high temperatures: low volatility species were condensed similarly and are re-emitted similarly (no important mixing effect).

Second, the zone were two TGAs differ is always approximately 40°C after the TGA on the warmest QCM starts. In the same zone it can also be noticed that the first 30°C of each TGA gives no emission at all (up to experimental uncertainty). The explanation is quite straightforward. A QCM that spend 24 hours e.g. at 0°C was subject to some evaporation. At the TGA start, the crystal remains a few minutes in the [0-30°C] range. Hence evaporation is only possible for molecules of which residence time at 30°C is less than a few minutes. However they previously spent 24H at 0°C and are only present at TGA start if their residence time at 0°C was longer than 24H. So this "blind zone" of 30 or 40°C at the start of the TGAs is explained by re-emission before the TGA, and it can be checked that its size is consistent with typical activation energies (a 24H residence time become on the order of the minute for a temperature increase close to 30-40°C).

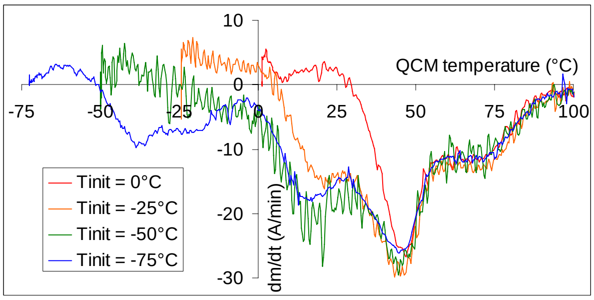

Fig. 21. TGAs performed on four QCMs (at 2K/mn) which were initially submitted to the same contaminant flux while being maintained at four different temperatures (ECC2216, ESA TRP, ONERA data).

This clearly explains the observed difference between the TGAs at the beginning of the one from the warmest QCM. So if the first 40°C of a TGA is excluded we can conclude (on this example) that a TGA from a warmer QCM does not provide more information than a TGA from a colder QCM since it can simply be deduced from the latter. If this result is confirmed on other materials, its will have important practical consequences. Only one cold QCM may be needed and its TGA should allow determining what would be the deposit at another temperature.

The theoretical aspects of this result are also interesting. Although this is certainly not true at detail level, this shows that (on this case) mixing effects are not very important. For example the presence of the species evaporated around -40 on "the -75° QCM" were not present on the "the -50° QCM". However the evaporation of other species around +10-20°C is unaffected. Of course such mixing effects are more likely to show up for species with closer evaporation temperatures.

7. CONCLUSIONS AND PERSPECTIVES

We reviewed the physical grounds of contamination and the two major approaches to its practical assessment, either empirical or physical. We next discussed the questions still open to improve and validate the ambitious physical approach. We finally presented some original results stemming from important recent efforts in Europe to validate this approach.

The most notable conclusions are the predominance of the desorption limitation over the diffusion limitation in outgassing, and a rather "linear behaviour" of deposits in TGAs (little mixing effect, independence of re-emission of different species). Of course these facts are not universal since the phenomena that appear negligible in our data (limitation by diffusion and mixing effects) are perfectly known to exist elsewhere. However in an engineering context a gradation of the relative importance of diverse phenomena is very valuable. Unfortunately, estimating the validity range of such "judgements" remains difficult. Doing so empirically by extensive testing is costly, while doing so on theoretical grounds is difficult but may be an interesting idea.

The European efforts in the last years aiming at validating a physical and practical approach to contamination were in the result of a close collaboration between CNES, ESA and ONERA. They involved activities in all companies, the ones at ONERA being funded by CNES R&T and ESA TRP, for which ONERA authors are grateful to CNES and ESA. The next major outcome of these still ongoing activities shall be an upgraded routine test procedure. It shall at least involve TGAs at the end of each temperature step for a refined characterisation of the species outgassed over time. The numerical tools used for the analysis of these data will also need a significant upgrading.

7. REFERENCES

1. Van Eesbeek M. and Zwaal A, Outgassing and contamination model based on residence time, *Proceedings of the 3rd European Symposium on Spacecraft Materials in Space Environment*, ESTEC, Noordwijk, The Netherlands, pp 25-34, 1985.

2 Nghiem M.P., Tondu T., Chardon J.-P., Faye D., Roussel J.-F., Parametric study of molecular contaminants sticking enhancement under UV irradiation, this conference.

3. Pereira A.., Roussel J.-F., Van Eesbeek M., Schmeitzsky O., and Faye D., Experiments and physical modeling of ultraviolet-enhanced contamination from pure contaminants. *Journal of Spacecraft and Rockets*, Vol. 43, No. 2, pp 402–409, 2006.

4. Roussel J.-F., Alet I., Faye D., and Pereira A., The effect of space environment on spacecraft surfaces on sun-synchronous orbits, *Journal of Spacecraft and Rockets*, Vol. 41, No. 5, pp 812-820, 2004.

5 ASTM E 1559, Standard Test method for Contamination Outgassing Characteristics of Spacecraft Materials, , ASTM committee E-21, 1993.

6. Roussel J.-F., Lemcke C., Giunta I., Van Eesbeek M. and Sorensen J., Contamination Modelling: Underlying Principles and First Examples for a New Software, *8th International Symposium on "Materials in a Space environment"*, Arcachon, France, 5-9 June 2000.

7. Brunauer, S., Emmet, P. H., and Teller, E., Adsorption of gases in multimolecular layers, *Journal of the American Chemical Society*, Vol 60, pp 309-319, 1938.

8 Bargeron C. B., Phillips T. E. and Benson R. C., Thermogravimetric Analysis of selected Condensed Materials on Quartz Crystal Microbalance, SPIE vol. 2261, pp188-199.

9 Tondu T, Nghiem M.-P., Chardon J.-P., Roussel J.-F. and Faye D., Thermogravimetric analysis for characterization of molecular contaminants irradiated by UV, this conference.