

Char and Erosion Factors with Reference to Phenolic Matrix Composites

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February 2011

Physical vs. Chemical Erosion Factors

Any and all gaseous products presented in the following sections, as well as their intermediary radical forms, could be considered as potential candidates for *chemical* erosion of exposed SRM material surfaces. However, alumina (Al_2O_3) is the major constituent comprising the slag phase during aluminum-fueled burn cycles, and is considered to be the primary culprit responsible for *physical* erosion of the liner materials, particularly those in the aft regions of the motor where the Al_2O_3 particle concentration is greatest. Note that above about 3700°-3800°F, Al_2O_3 particles will melt, altering the erosion patterns they might produce in the highly abrasive solid state. Thus, during an SRM cycle, molten Al_2O_3 particles and their agglomerates are the principal species leading to physical erosion. It should also be noted that alumina is a *glass-ceramic*. At lower static temperatures (2000°-2500°), solid Al_2O_3 particles will coalesce or *sinter* together to form larger agglomerates or ceramic bodies. Above about 5400°, alumina will vaporize where its physical erosion properties vanish. One could argue that between ~3800°-5400°F, the possibility for *chemical* interactions between Al_2O_3 and the liner materials is greatest.

However, Al_2O_3 is generally quite inert. The conditions and supporting environment must lead to the *liberation* of Al atoms from the Al_2O_3 structure. Exposed Al is a strong reducing agent. It is looking for oxidizing groups or compounds to react with. The as-cured phenolic network contains a few hydroxyl -OH and ether -O- groups which could conceivably provide a limited degree of redox potential to support such activity. Additionally, the Al atom tends to form coordination links with certain organic species. In our situation, carbon monoxide (CO) is quite abundant throughout the system and within the degrading liner material. It is well known that CO is a very strong ligand. One might expect to find trace levels of complexed aluminum in the char (if the above arguments are true). With respect to the carbon fibers and the phenolic matrix phase *after* it carbonizes, molten aluminum carbide (Al_4C_3) might form which could conceivably participate if further chemical/physical erosion effects down-line. However, since Al_2O_3 is essentially an inert ceramic to begin with, the entire scenario of possible chemical reactions involving alumina with any of the insulation materials could probably be considered irrelevant . . . especially when compare to the abundance of bombarding pyrolytic (chemically eroding) products generated throughout the material decomposition process.

Thermal Redox in an SRM Environment

During a typical SRM burn cycle, the level of free oxygen available at the material surfaces is expected to be relatively low. Exposed materials will undergo essentially anaerobic pyrolysis or *partial* oxidation (incomplete combustion). Leading products in the partial oxidation of organic matter will always include high levels of H_2 and CO along with small molecular hydrocarbons such as methane, ethane and their radicals (benzene and methyl-substituted benzenes will be generated from aromatic substrates such as crosslinked epoxies, esters and phenolic networks). Intermediary products of partial combustion may also include formaldehyde ($\text{H}_2\text{C}=\text{O}$), hydrogen peroxide ($\text{HO}-\text{OH}$) and their radical forms (hydrocarbonyl and peroxy). Note that most of these intermediates are still flammable downline or in the main plume. Many can act as reducing agents (especially at elevated temperatures) as they undergo full oxidation to CO_2 and H_2O . In sulfur-vulcanized aliphatic elastomers, (such as SBR), smaller levels of SO and SO_2 will also be generated, and in nitrile rubbers (i.e... NBR), emissions of both SO_x and NO would be expected (both of which can act as reducing agents). In any kind of burning event, if appreciable levels of either H_2O or CO_2 happen to stagnate or make their way back to the flame interface, they will

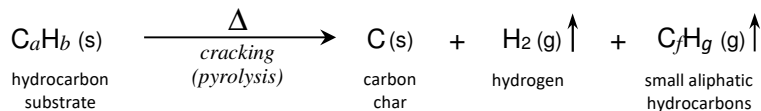
tend to extinguish to the flame. It is interesting to note, flaming combustion produces its own extinguishers and the burning process is sustained only as long as there is a mechanism in place that rapidly transports the extinguishing species away from the burn zone.

Further down and out of the burn zone within the nozzle exit cone cavity, there is even less available oxygen. Here, the vapor layers interfacing the ablating surfaces are essentially starved of oxygen since none is generated from local fuel reactions in this area and the majority of oxygen produced in the motor case section is consumed before entering the exit cone region. Considering the possible products and species generated during the overall burn process, the plume will likely contain a mixture of both oxidizing and reducing agents of varying strengths and concentration levels. So does the nozzle chamber become an oxidizing or reducing environment during a burn cycle? The answer likely includes both. There may be localized regions where atoms/molecules comprising the ablating materials undergo oxidation (loss of electrons) and other areas where reduction predominates (gain of electrons). Overall, the burn environment in the nozzle section probably favors reduction while both processes may be occurring concurrently.

Overall, the motor volume could perhaps be effectively characterized as a *depleted* oxidation environment. Oxidation of the material will almost always lead to chemical erosion, but this is not necessarily the case for reduction reactions (in general, oxidation degrades or disintegrates the material while reduction is sometimes likened to a building process). Under *static* burn conditions, the data clearly indicates that oxidative chemical erosion of char-producing substrates is generally insignificant [1]. Consider the idea that within a typical SRM environment, the hot blasting forces are so intense, that even a very small level of weakly oxidizing species present within the high energy plume can result in substantial material losses. Overall, ablation in such systems might occur as a result of two major contributions: thermophysical abrasion due to high energy particle impingement and physicochemical erosion brought about as small, localized streams of weak-to-moderate oxidation agents are forced into and along the surface boundaries of exposed substrate materials.

Pyrolysis/Combustion Reactions and Mechanisms

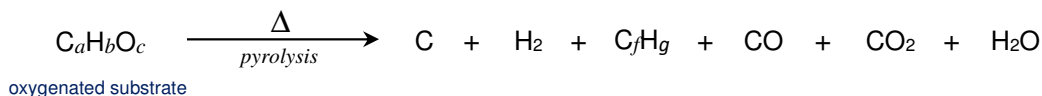
There is ample information available detailing the reaction kinetics, mechanisms and thermodynamic factors for classical processes involving the thermal oxidation, combustion and pyrolysis of organic materials into CO₂ and H₂O. There is no reason to duplicate all those concepts here. However, it might be interesting to explore some of the partial oxidation aspects of these processes in greater depth. For starters, consider the anaerobic pyrolysis of simple hydrocarbon-based materials under static conditions (oxygen-free thermal cracking). A generalized (unbalanced) representation of the *overall* reaction might show a product mix containing carbonized substrate (solid char remnant), molecular hydrogen and small gaseous hydrocarbon molecules . . .



For the majority of polymers used in industrial and everyday products, including elastomers and conventional binders used in adhesives, coatings and low tier composites, the chains and structures are easily disintegrated when exposed to pyrolytic temperatures, volatilizing into H₂ and small hydrocarbons (methane, ethane, ethene, etc...) with little residual char produced (that is, [C] ~ 0 in the above equation). Additionally, H₂O, CO₂ and CO are produced in quantities that are related to the amount of oxygen present in the flame environment (if any) *and* within the substrate as water previously absorbed from the environment and/or chemically bound within the polymer structure. In general, most of the common polymers are hygroscopic to varying degrees, containing appreciable levels of oxygen and water, both physically and chemically bound. Thus, even under anaerobic pyrolytic

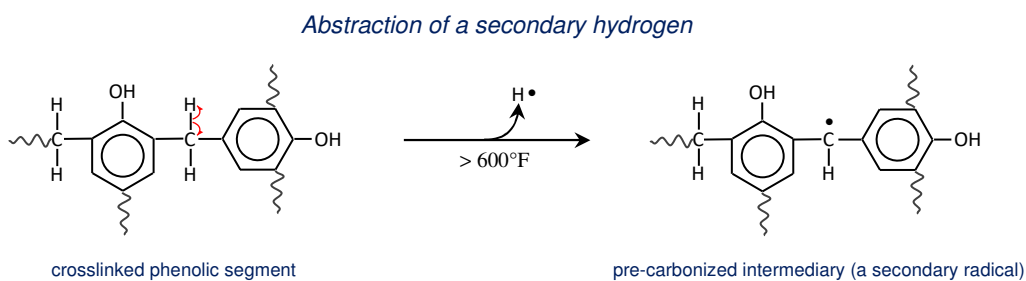
All technical descriptions, chemistry and illustrations in this paper are the interpretation and handiwork of the author except where noted.

conditions, some oxidation of the material is unavoidable as the oxidizer can come from within the material. Lower levels of intrinsic oxygen imply burn processes where incomplete combustion is taking place, accompanied with the release of CO. In any event, the product gases will also include lower levels of CO₂ and H₂O, corresponding to instances or locations where full oxidation takes place. Overall, one could write . . .

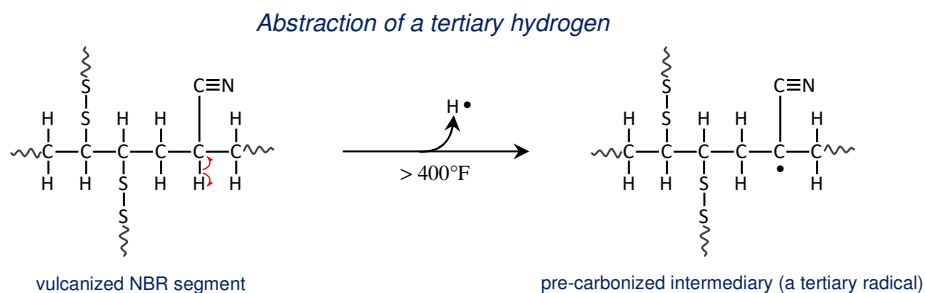


In addition to H•, some of the more prominent gaseous radicals generated in these reactions which propagate the pyrolysis process include hydroxy HO•, formyl HOC•, peroxy HOO• and atomic oxygen •O, a diradical. As with molecular dioxygen O₂, ground state oxygen atoms are triplet state paramagnetic diradicals which can be excited to metastable singlet states under certain conditions. For this study however, triplet state oxygen atoms are considered to be the principal culprit involved in the oxidation and erosion of materials in the SRM burn/blast environment.

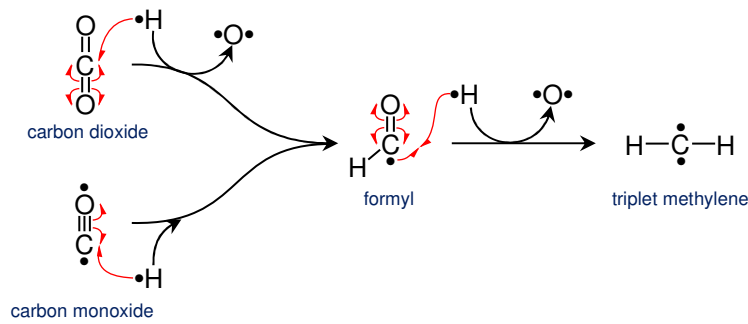
It should be obvious at this point that, in general, the thermal conversion of organic matter into volatiles and carbon char is a *free radical-driven process* involving an array of possible chain reaction sequences, be it flaming combustion, pure anaerobic pyrolysis, static or dynamic oxidation. When heat degrades these materials, the chemical bonds joining adjacent atoms along the polymer chains are cleaved into segments while the pairs of bonding electrons are split homolytically between the separating atoms. For example, when the level of heat absorbed within a crosslinked phenolic network reaches the effective bond dissociation energy of a secondary methylene carbon-hydrogen bond, scission occurs in which one electron is retained by each fragment – the phenolic substrate and the released hydrogen atom (recall that a single hydrogen atom is a free radical). With numerous radical sites along the chains at any given time, the substrate becomes a very reactive paramagnetic radical with each lone electron occupying a singly occupied molecular orbital (SOMO) . . .



In branched structures (most polymer systems of interest), these unpaired radical electrons will almost always rearrange or shift around to other atoms along the structure resulting in radicals with greater stability, lower energy and increased reactivity. Tertiary and secondary hydrogens are often the first H-atoms generated during a burning event (they are easy to abstract and represent stable radicals). For example, during the early decomposition of crosslinked nitrile rubber (NBR) polymers, tertiary radicals could be the first intermediates produced . . .



Radical-induced formation of triplet state paramagnetic methylene diradicals from carbon dioxide and carbon monoxide



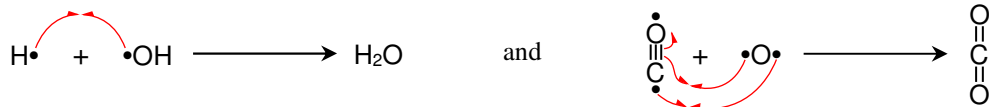
Note: Methylene is the precursor to *methane* and is the building block to larger carbenes, alkanes and alkenes that may form during pyrolysis.

Again, there are literally hundreds of likely chain reaction steps occurring throughout the burn process, and even more for polymers containing nitrogen and sulfur groups. However, within cooler regions of the flame or plume as well as when the burn cycle begins to subside, a number of termination and recombination reactions are taking place which ultimately lead to the formation of the (non-radicalized) molecular species produced and detected during pyrolytic burning events. Some of the more relevant termination reactions might include . . .

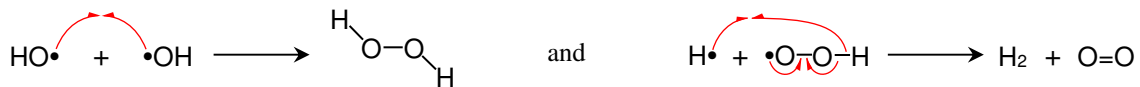
Combination of hydrogen atoms to give molecular hydrogen and the combination of atomic oxygen to give triplet molecular oxygen



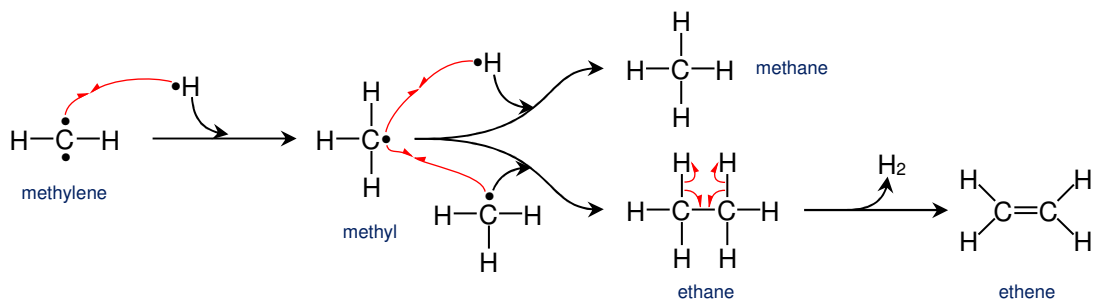
Combination of hydrogen with hydroxy to give water and the combination of carbon monoxide with atomic oxygen to give carbon dioxide



Combination of hydroperoxy to give hydrogen peroxide and the combination of hydrogen with hydroperoxy to give molecular hydrogen and molecular oxygen



Combination of hydrogen with methylene to give methane and the combination of methyl radicals to give ethane and ethene



Note 1 : It should also be realized that in perchlorate-based SRM fuel mixtures, free radical chlorine atoms are ever present to participate in reactions with other radical species, the most obvious being combination with hydrogen to form gaseous hydrogen chloride . . . $H\cdot + \cdot Cl \longrightarrow HCl$.

Note 2: In cooler regions and when the burn process begins to subside, most of the triplet carbon monoxide $\cdot C\equiv O\cdot$ will have a tendency to decay to it's non-radical singlet ground state $:C\equiv O:$ perhaps by triplet-singlet inter-system crossing with phosphorescence . . . $\cdot C\equiv O\cdot \longrightarrow :C\equiv O: + hv$.

Note 3: There is so much CO generated in these types of processes that a substantial portion does not even enter into any of the chemical reactions and is liberated throughout the process. Both triplet and singlet CO are expected to be released (at least initially) during an SRM burn cycle.

Note 4: In a typical Shuttle-type SRM chamber near the peak of a burn cycle ($\sim 5500^\circ F$, ~ 900 psi), it could be surmised that $n_2/n_1 \sim P_2/T_2(P_1/T_1)^{-1} \sim 5$ which implies that there is a five-fold increase in the number of molecules (this of course neglects the volume change as the fuel is consumed).

All these products and intermediates become potential agents for the chemical erosion of liners and substrate materials which are exposed to the flame and blasting forces. The preceding discussion explored some of the more prominent reactions associated with pyrolysis and conversion of organic matter into the volatile species which are known to be generated during partial oxidation burning events but has not considered any of the reactions taking place in the solid state phase . . . which involves the formation of inorganic carbonaceous char.

Production of Solid Pyrolytic Char and Char Yield

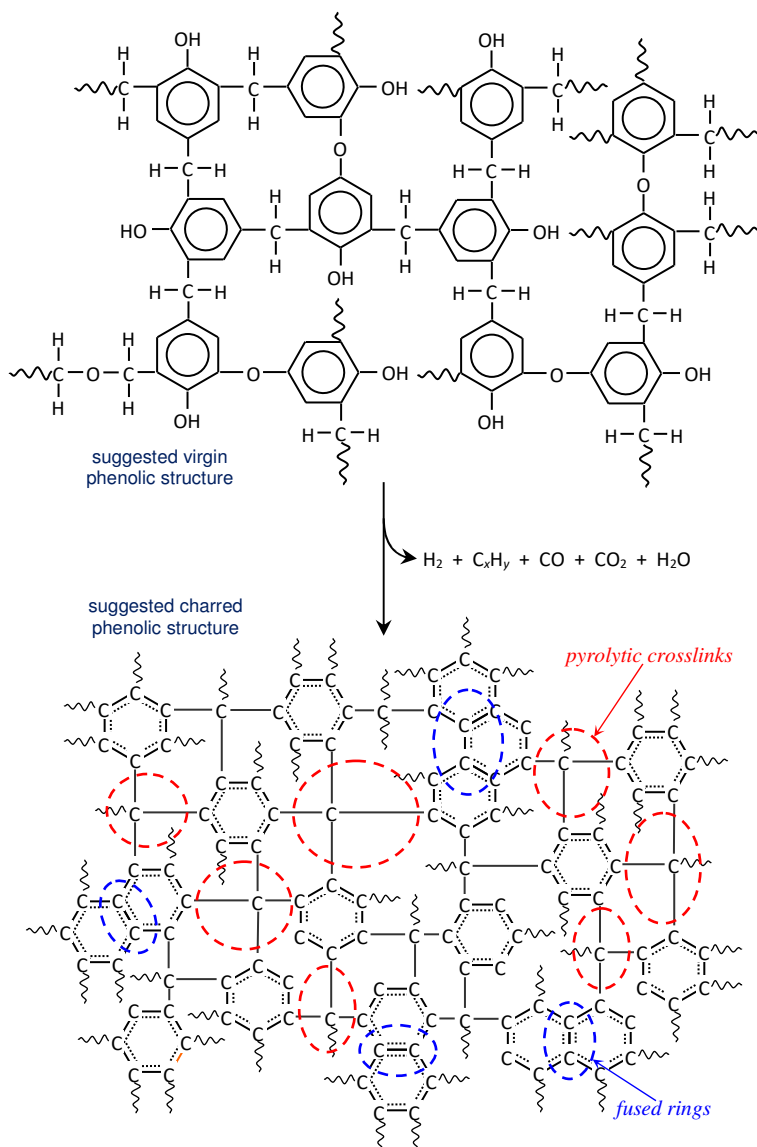
It is interesting to reiterate here that during static pyrolysis and combustion events, almost all thermoplastics and some of the thermoset materials we are familiar with produce very little char upon firing, often less than 10%. A surprising number of common polymers yield no char residue at all as the material is completely volatilized by the heat (oxygen and blasting forces not required). A few of the more well known polymers (non-crosslinked thermoplastics) which have been shown to yield 0% char upon pyrolysis include ^[5] polyethylene (LDPE), polypropylene (PP), polytetrafluoroethylene (PTFE – Teflon), polymethyl methacrylate (PMMA), polystyrene (PS), polycaprolactam (Nylon 6), styrene butadiene rubber (SBR), polyacrylonitrile butadiene-styrene (ABS), and of course, nitrile butadiene rubber (NBR), but there are many more. Some of the familiar thermoplastics yielding > 0% but < 5% char remnant include polyvinyl alcohol (PVOH), polyvinyl acetate (PVAc), polyethylene terephthalate (PET) and bisphenol-A epoxy (Dow DER-332). The halogenated analogs of some of these polymers can give > 10% char yield. Examples include polychloroprene (Neoprene), polyvinyl chloride (PVC) and chlorosulfonated polyethylene (Dupont's Hypalon®). In these systems, the pendant halogen atoms act as flame retardants which increase the char yield (. . . the higher the char yield, the lower the flammability).

Some of these thermoplastics can be tailored to incorporate crosslinks which are generated during a second stage curing process to give network polymers that are either (1) lightly crosslinked, (2) moderately crosslinked or (3) heavily crosslinked. Crosslinking will invariably increase their char yields. The NBR polymers of interest in our study fall into category (1) and are not really qualified to be called 'thermosets'. While a few fragments of the lightly vulcanized NBR may survive static pyrolysis, it is not realistic to consider this material a char-producer and certainly not an ablative as it is destined to be consumed during the burn process. In contrast, the highly crosslinked phenolic structure yields over 50% char and loses about the equivalent of all the hydrogens and hydroxy groups within the structure as the network of strong crosslinks retards main chain depolymerization and decomposition.

In further contrast, mesogenic structures and liquid crystal polymers often have minimal hydrogen and oxygen content within their structures and thus, many LC materials provide impressively high char yields. For example, PBI (polybenzimidazole) and PBO (polyphenylene benzobisoxazole) give around 70% char yield, Dupont's polyphenylene isophthalamide aramid 50% char yield, Ciba's F-10 cyanate ester 55%, GE's BPCPC bisphenol-C polycarbonate 50%, Amoco's polyamideimide (Torlon) 55%, Victrex's P22 polyetherketone (PEK) 53% and Madem's X-1000 polybenzoyl phenylene 65%. There are many more, and there are a number of similar LC research polymers which are on the brink of commercialization including UMASS' polyazomethine which yields ~78% char and the Navy's biphenol phthalonitrile at 79%. Though not well publicized, a couple of polymer

classes, the polyarylacetylenes and polyalkynyl cyclopentadienes can yield > 85% char. These would be some interesting polymers to experiment with for potential development of advanced carbon fabric / polymer matrix rocket liners, polymer-impregnated ablators and next-generation carbon/carbon composites.

As inferred earlier, one of the key factors leading to high char yields is the formation of advanced sp^2 - sp^3 bonded pyrolytic crosslinks during the decomposition phase of the burn process. In addition, the char consolidation process is greatly facilitated, particularly in high aromatic structures, by the fusion of sp^2 -bonded benzene rings. It is surmised that the original thermoset crosslinks ‘hold’ the polymer structure in place (preventing disintegration and volatilization) while facilitating the formation of high temperature pyrolytic links and fused rings which connect neighboring radical sites together. An illustration of this can be visualized by considering representative configurations of the virgin phenolic structure and it’s fully charred conversion product * . . .



Ring fusion also occurs in aromatic thermoplastics as they pass from their mesophase state into green carbonaceous char where the absence of pyrolytic links permits easy transformation into the 3-D graphite structure later on (4200°- 4500°F). These high temperature crosslinks are the principal attribute responsible for the formation of non-graphitizable glassy carbons. There is much evidence that the green carbon forms derived from

* All reactions, mechanisms, theories and representative chemical structures provided throughout this report are the perceptions and opinions of the author. No guarantee is made regarding their accuracy or correctness.

thermoplastic-based mesophase structures are entirely bonded via sp^2 hybridization, leaving the pool of pi electrons free to influence material properties such as conductivity effects. In contrast, thermoset-derived glassy carbons are believed to contain a mixture of sp^2 and sp^3 bonding orbitals throughout the structure. This corresponds to the well documented attributes for glassy carbon of low conductivity with glassy/amorphous ceramic-like properties.

Physicochemical Erosion of Composites and Their Constituents

The kinetics of chemical erosion of nonmetallic nozzle materials has been well documented. It is not the intent here to duplicate any of those efforts but to expand or elaborate and propose some additional insight that may help account for the chemical loss of exposed materials and structures during the burn cycle of a typical SRM. For motors based on aluminum fuel, flame temperatures have been reported as high as $\sim 5500^\circ$ - 6000°F . During the burn cycle, aluminum oxide (alumina) is produced in abundance (Al_2O_3 , m.p. $\sim 3760^\circ\text{F}$, b.p. $\sim 5400^\circ$). Also, certain flame-exposed insulator/ablative components and liner structures in the SRM systems of current interest (such as PBI/NBR composite) contain particles or fibers of silica (SiO_2 , m.p. 2900° - 3200° , b.p. $> 4000^\circ$), and once this silica is dislodged from the composite material, it becomes part of the particle stream or slag. However, relative to the level of alumina, the quantity of silica in the flame is minuscule.

Thus, in these systems, physical erosion is due almost entirely to the ablative action of high energy impacting Al_2O_3 particles. However, in regions of the flame that surpass about 3800° - 3900°F , the alumina particles are expected to be in the liquid state and their erosion properties are diminished accordingly. It is presumed that the melting points for these types of oxide ceramics (aluminas and silicas) are elevated under increased pressures in accordance with Simon's equation^[7] . . . $a(P - P_p) = (T_m - T_m^{1atm})^b - 1$. Thus, in aluminum-fueled systems, physical erosion is expected to impart the greatest degree of material damage earlier in the burn cycle. It is feasible that chemical erosion could affect certain constituents anywhere above about 700° - 800° , but it is probably during the peak of the cycle when chemical erosion effects are maximum as the erosive agents are chemically energetic and physically driven onto/into the material surfaces by the hot blasting forces. It is also presumed that, at the lower temperatures, chemical erosion is kinetic-dominated but at the higher temperatures when the density of reaction products in the plume is highest, erosion reactions probably become more diffusion-controlled. Bear in mind that chemical and physical erosion are in addition to and may be coupled with the temperature-driven processes of pyrolytic char formation and volatilization since for much of the burn cycle, they occur simultaneously.

It may also be feasible to presume that charring, carbonization and/or volatilization of flame-exposed virgin material surfaces has already progressed to a significant extent before the degree of chemical erosion reactions become pronounced. Thus, char-producing polymer constituents (such as phenolic and PBI) are essentially in a pyrolyzed carbon state when erosive effects reach their most aggressive stage, while volatilizing constituents (NBR, EPDM, etc...) have all but vanished. This implies that, for the most part, chemical erosion reactions are essentially occurring on *carbonized* surfaces of the substrates. For example, exposed surfaces of carbon fiber / phenolic matrix composite structures may already be in a carbon-carbon state before the damage from chemical erosion reactions becomes substantial. Erosion of PBI/NBR structures is trivial since the primary binder (NBR) is volatilized and blown away during the early pyrolysis phase. However, protruding PBI fibers whose roots remain embedded in the virgin NBR phase will themselves produce high char yields and are also subject to chemical erosion forces. The effects and consequences associated with physical particulate erosion are topics for another study.

Now if chemical erosion is considered to be primarily an oxidation process, then even small levels of weak-to-moderately oxidizing species under the turbulent thermophysical action and high pressures of the plume can lead to substantial material losses through physicochemical ablation. The strongest oxidizers in this series might exhibit effective thermal oxidation strengths according to $\bullet\text{O}\bullet > \text{HOO}\bullet > \text{HO}\bullet > \text{CO}_2 > \text{H}_2\text{O}$. However, in terms of the

If erosion-driven pyrolytic links also form during the thermal conversion of PBI fibers, then glassy-like regions may develop in the periphery of these structures as well and these regions will tend to retard graphitization in the upper temperature regimes (after exposure to > 4000°F erosion, the fibers may contain regions that are both glassy-like and graphitized). The preceding illustrations and ideas are proposed only to indicate the basic reactions that might describe oxidation-based erosion of the concerned materials and are not intended to imply anything about the relative erosion rates. Obviously, carbon fibers, phenolic matrices and PBI phases exhibit much lower erosion rates than soft polymers such as NBR and EPDM which would erode very quickly if they survived the pyrolysis heat. It could be presumed here that the erosion reaction scenario tends to follow first order kinetics while the erosion recession process conforms to a para-linear parabolic law, but these are topics for another study.