Mechanisms and Models of Solid-Propellant Burn Rate Temperature Sensitivity: A Review

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Nomenclature

A_s = kinetics prefactor for propellant gasification
c_p = specific heat
E_g = activation energy of controlling gas-phase reaction
E_{PF} = activation energy of primary diffusion flame reaction
E_s = activation energy of propellant gasification
n = burning rate pressure exponent
N = order of gas-phase reaction
Q_s = net heat of gasification (exothermic is positive), also Q_L
$\bar{Q}_s$ = average value of Q_s between HMX and binder in composite modified double-base (CMDB) propellant
r = burning rate
r_{DB} = burning rate of energetic binder in CMDB propellant
R = universal gas constant
T_0 = propellant bulk, or conditioning temperature
T_F = flame temperature
T_s = propellant surface temperature
X^*_{PD} = diffusion flame height
X^*_{PF} = reaction length component of the diffusion flame
Φ = heat feedback flux to the propellant
Φ_{comb} = portion of Φ due to the combustion process
Φ_{ext} = portion of Φ due to external influences
π_k = temperature sensitivity of pressure at constant K_n
$\pi_{p/r}$ = temperature sensitivity of pressure at constant p/r
ρ_p = propellant density
σ = particle size distribution width parameter
σ_p = temperature sensitivity of burning rate at constant pressure
ξ = dimensionless flame height
ζ = parameter related to AP volume fraction in a CMDB propellant

Introduction

THE response of solid-propellant ballistic properties to changes in propellant bulk temperature (conditioning temperature) has received an increasing amount of attention in recent years. The renewed interest has been stimulated by modern propulsion requirements and the recognition that temperature sensitivity is one of the aspects of propellant combustion mechanisms as well as ballistic properties tailoring. This paper presents a literature review of the mechanisms affecting temperature sensitivity in terms of the published combustion models embodying those mechanisms.

There are four categories of mechanisms that affect temperature sensitivity. The first type, which comprises the bulk of the paper, is the collection of straightforward mechanisms that are treated in analytical models. These include the rise in the propellant temperature to its surface temperature and the heat feedback from the flame. The second type is the collection of nonideal and complex facets of the combustion process that are not normally treated in models. Examples include surface chars and melts, aluminum agglomeration, nonuniformities on various scales, and certain ingredient interactions. Not enough is known about their effects on temperature sensitivity to be a subject for review. The third type comes under the general heading of shifts in the controlling mechanisms, some of which are treated in models. These shifts normally manifest themselves by changes in pressure exponent that, as a result, also bring about changes in temperature sensitivity. Perhaps the most notorious example is the onset and loss of catalysis, as in mesa propellants, but shifts in the controlling flame structure have been modeled more extensively. The fourth mechanism covers the effects of a motor environment, of which erosive burning has been studied the most extensively.

Fundamental Considerations

Raising Propellant Temperature to the Surface Temperature

The simplest and perhaps most fundamental analysis of temperature sensitivity was discussed by Glick.[1] An energy balance at the propellant surface yields

$$\rho_p c_p r(T_s - T_0) - \rho_p r Q_s = \Phi \tag{1}$$

Assuming constant values of c_p, T_s, Q_s, and Φ, differentiation of Eq. (1) yields

$$\sigma_p = 1 \Big/ \left(T_s - T_0 - \frac{Q_s}{c_p}\right) \tag{2}$$

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Several important trends are apparent from this simple expression. For low σ_p, it is desired that the surface temperature be high and that the heat of gasification be negative (endothermic). Since the surface temperature tends to increase with the burning rate and pressure, propellants with higher burning rates and higher pressures should promote lower σ_p. The expression also indicates a decrease in σ_p with decreasing temperature. That propellants with higher burn rates tend to have lower temperature sensitivity is evident in data, at least as a gross generality. Lower temperature sensitivity in the data can also be associated with higher surface temperatures. There is no present consensus on the ascertainment of values of Q_s, but reasonable interpretations can associate higher temperature sensitivity with an exothermic condensed phase. However, the effects of pressure and temperature are not as systematic as might be inferred from Eq. (2).

More elaborate analyses relax the assumptions of constant T_s and constant Φ. Varying expressions for Φ and the resulting temperature dependence are the chief distinguishing features among the various combustion models that have been developed. With few exceptions, however, the thermal properties are assumed to be constant in the models. Accounting for the temperature dependence of thermal properties is important for improved temperature sensitivity analysis.

Sensitivity of Regression Rate to Surface Temperature

The regression of the burning surface is generally assumed to follow an Arrhenius law,

$$r = A_s \exp(-E_s/RT_s) \tag{3}$$

Taking into account this dependence of rate on surface temperature, Eq. (2) becomes

$$\sigma_p = 1\Big/\left[\frac{RT_s^2}{E_s} + \left(T_s - T_0 - \frac{Q_s}{c_p}\right)\right] \tag{4}$$

The equation suggests that a low activation energy of decomposition would tend to reduce σ_p. However, substituting numbers that are ordinarily seen in combustion modeling work reveals that the new term in the denominator is typically an order of magnitude smaller than the original group of terms. Thus, it is a small correction to the result.

Simplified Heat Feedback Models

GDF or KTSS Model

Ewing and Osborn[2] and Cohen-Nir[3] derived expressions for σ_p based upon the Summerfield granular diffusion flame (GDF) model of composite-propellant combustion. This model has also come to be known as the KTSS model as a result of a series of papers in which the GDF model represented the heat feedback law in studies of nonsteady combustion processes.[4-6] An important result of those studies was that high temperature sensitivity would promote a stronger response to disturbances, unstable burning, dynamic overshoots, and extinguishment.

The difference between the Ewing and Osborn and Cohen-Nir expressions stems from the fact that Ewing and Osborn retained the constant surface temperature assumption, whereas Cohen-Nir incorporated the Arrhenius law. The differences in Eqs. (2) and (4) stem from the fact that Φ is no longer a constant. The Cohen-Nir expression is

$$\sigma_p = 1\Big/\left[\frac{RT_s^2}{E_s} + 2\left(T_s - T_0 - \frac{Q_s}{c_p}\right)\right] \tag{5}$$

It should be pointed out that the gas temperature and gas thermal properties were assumed constant in the analysis; earlier remarks regarding temperature-dependent thermal properties are also applicable here. For typical values of the parameters as applied to AP composite propellants ($E_s = 22{,}000$ cal/mole, $T_s = 900$ K, $T_0 = 298$ K, $Q_s = 40$ cal/g, $c_p = 0.3$ cal/g·K), $\sigma_p = 0.10\%/°\text{C}$. This is a low, but plausible, result.

Difficulties were encountered when attempting to apply the GDF model to the temperature sensitivity data. There were deviations between the trends predicted by the model and the data.[2,3,7] This is not to fault the model, but to recognize that simplifications may not be able to get at the specifics of the combustion behavior of real propellants.

Denison and Baum Premixed Flame Model (Coates)

By suitable manipulation, it is possible to express σ_p in terms of gas-phase parameters rather than solid-phase parameters. This was done by Coates in applying a laminar flame theory to the question of temperature sensitivity.[8] For constant and equal specific heats in the gas and in the solid, the theory yields

$$\sigma_p = \frac{1 + (N/2)}{T_F} + \frac{E_g}{2RT_F^2} \tag{6}$$

Of course, the gas and the solid phases need to be consistent with one another, as matched by the energy balance at the surface boundary.

From the standpoint of the gas phase, it is observed that low σ_p is promoted by a high flame temperature (more energetic propellant), low activation energy of the gas-phase reaction, and low reaction order. It is generally true, at least in a gross sense, that more energetic propellants tend to have lower temperature sensitivity. For typical values of the parameters associated with AP composite propellants ($N = 2$, $T_F = 3000$ K, $E_g = 15{,}000$ cal/mole), $\sigma_p = 0.11\%/°\text{C}$. This is consistent with the Eq. (5) result.

Kubota Energetic Binder Model

Kubota[9] developed a model for the combustion of energetic binders based upon application of Schvab-Zel'dovich flame theory to the fizz zone in the gas phase. The result was a closed-form expression for the burning rate in terms of both gas- and solid-phase parameters. This expression can be differentiated for σ_p. The result is

$$\sigma_p = 1\Big/\left[\frac{RT_s^2}{E_s} + 2\left(T_s - T_0 - \frac{Q_s}{c_s}\right)\right] + \frac{E_g}{2RT_F^2} - \frac{1}{T_F} \tag{7}$$

It is evident that certain groups of terms are recurring in these analyses; they are fundamental aspects of temperature sensitivity. For reasonable values of the parameters as associated with energetic binders ($E_s = 40{,}000$ cal/mole, $T_s = 650$ K, $T_0 = 298$ K, $c_s = 0.4$ cal/g·K, $Q_s = 100$ cal/g, $E_g = 16{,}000$

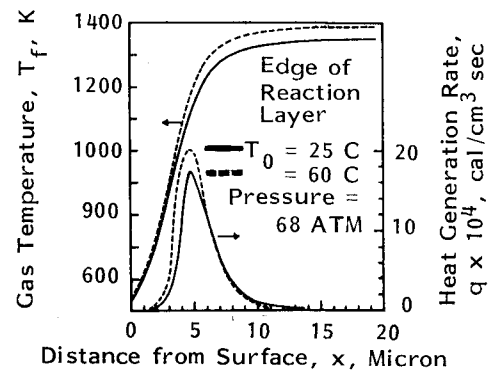

Fig. 1 Calculated effect of T_0 on the gradients in the fizz zone.[10]

cal/mole, $T_F = 1600$ K for the fizz zone), $\sigma_p = 0.54\%/°C$. This is a very reasonable result for the σ_p of an energetic binder.

Figure 1 shows the important properties of the gas phase as a function of T_0 when accounting for the distributed reaction in the fizz zone.[10] The increase in the sensible enthalpy has caused the gas-phase reaction to occur closer to the propellant surface, with the result that the temperature gradient at the surface (heat feedback) is increased. Thus, the burning rate is increased. Note that the fizz zone flame temperature is also increased. There has to be some increase in the flame temperature as a result of the heat stored in the solid from the temperature conditioning. The shape of the heat generation curve and its impact on the temperature profile will be a strong function of E_g.

BDP Monopropellant Models

A series of papers by Beckstead and his co-workers applied a portion of the Beckstead-Derr-Price (BDP) model of composite-propellant combustion to the combustion of monopropellant components. The first paper applied the original BDP model to the combustion of AP and HMX.[11] The second re-examined the combustion of AP and HMX with an improved version of the model.[12] The third applied the same basic approach to model the combustion of XLDB energetic binders.[13] In this approach, the heat feedback from the gas phase is described by a flame sheet model.

The most recent expression for σ_p published by Beckstead for this sort of model is

$$\sigma_p = \left[\frac{E_g}{2RT_F^2}\frac{dT_F}{dT_0} + \frac{e^{\xi}/\xi}{2(T_F - T_0 - Q_s/c_p)}\right] \div \left[1 + \frac{RT_s^2}{2E_s}\frac{e^{\xi}/\xi}{(T_F - T_0 - Q_s/c_p)}\right] \tag{8}$$

This expression differs from the previous ones in that the dependence of T_F on T_0 is explicitly acounted for, terms involving the dimensionless flame height in accordance with the flame sheet model appear, and the parenthetic group of terms involves the heat buildup to the flame temperature rather than the surface temperature. Beckstead also presented more approximate expressions than this one, based upon numerical evaluation of the terms. The simplest expressions were for the limiting conditions of combustion control by the gas phase (gas-phase limiting condition),

$$\sigma_p = \frac{E_g}{2RT_F^2}\frac{dT_F}{dT_0} \tag{9}$$

and combustion control by an exothermic condensed phase (condensed-phase limiting condition),

$$\sigma_p = E_s/RT_s^2 \tag{10}$$

The former would occur at very high pressures, the latter at very low pressures. Note that a change in the controlling mechanism with pressure is implied.

Beckstead's original calculations for AP are shown in Fig. 2. The qualitative behavior is in excellent agreement with Boggs' data,[14] but the values are too high. Beckstead explained this discrepancy in his second paper.[12] Other workers would disagree with the use of an exothermic Q_s,[15] which here served to achieve high values of σ_p. It should be pointed out that Beckstead performed the calculations by computing the burning rate as a function of T_0 and not by using Eq. (8) or approximations thereof. He noted the importance of accounting for the temperature and pressure dependencies of T_F.

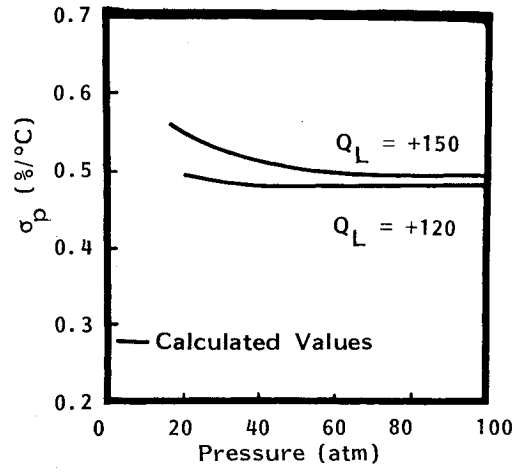

Fig. 2 Calculated σ_p for AP as a function of pressure.[11]

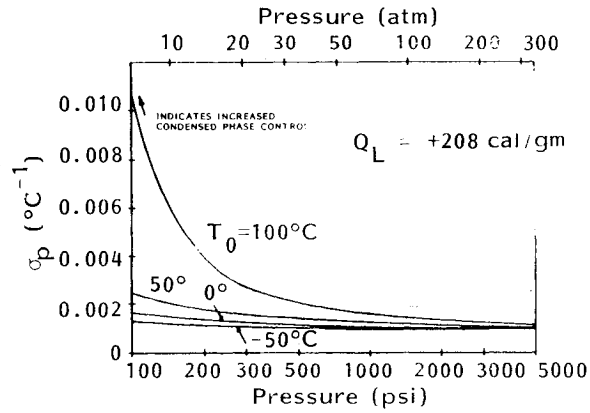

Fig. 3 Calculated σ_p for HMX as a function of pressure and temperature.[12]

Beckstead's calculations for the σ_p of HMX as a function of pressure and temperature are shown in Fig. 3. The pressure dependence is qualitatively correct, but the temperature dependence is not and the limiting value at high pressure is too high. Again, there would be an objection by other workers to the use of a highly exothermic Q_s.[15,16] Beckstead's calculations for XLDB energetic binders are shown in Fig. 4. The calculations provide the correct dependencies on heat of explosion, pressure, and temperature; the magnitudes are in the right range. Beckstead did use fizz zone flame temperatures in these calculations. His use of a moderately exothermic Q_s would be generally acceptable, but his choices for the kinetics constants would be open to question.[9,17]

Calculations by the authors for AP and HMX, using Eq. (9) and the values for the combustion constants they deemed appropriate, are as follows. For AP: $Eg = 15{,}000$ cal/mole, $T_F = 1430$ K, $dT_F/dT_0 = 0.8$, and $\sigma_p = 0.15\%/°C$. For HMX: $E_g = 16{,}000$ cal/mole, $T_F = 1900$ K (vapor-phase decomposition region), $dT_F/dT_0 = 0.4$, and $\sigma_p = 0.05\%/°C$. These values are the correct high-pressure values.

KTSS Form Applied to Nitramines

More comprehensive models for the combustion of AP, HMX, and RDX have been developed by Price, Boggs, and Derr[15] and by Ben Reuven and Caveny.[16] These models require numerical solution for the burning rate; a closed-form expression for σ_p cannot be derived. Price et al. did not use their model to calculate σ_p as such, but rather used σ_p and pressure exponent data to deduce values for the kinetics constants. Once obtained, the model calculations for the burning rate as a function of pressure and temperature were quite

good. The important conclusions of their work were that the gas phase is dominant at rocket pressures and that Q_s is net endothermic for AP and HMX. Cohen et al.[18] developed approximate versions of the Ben Reuven and Caveny model in which the model could be simplified and reduced to Kubota or KTSS forms. The results of applying Eq. (5) (KTSS form) to HMX and RDX at high pressure are as follows. For HMX: $E_s = 50{,}000$ cal/mole, $T_s = 800$ K, $Q_s = -100$ cal/g, $c_s = 0.4$ cal/g·K, and $\sigma_p = 0.06\%/°C$. For RDX: $E_s = 50{,}000$ cal/mole, $T_s = 650$ K, $Q_s = -150$ cal/g, $c_s = 0.5$ cal/g·K, and $\sigma_p = 0.08\%/°C$.

The value for HMX as derived from the condensed-phase properties is in close agreement with that derived from gas-phase properties. Surface temperatures were obtained from the thickness of the melt layers on extinguished surfaces and microthermocouple data.[19] They are somewhat different from the results of combustion model calculations, but there is little doubt from the data that the surface temperature of HMX is considerably higher than that of RDX. The net Q_s endothermicities are derived from literature data except that some deductions are required for the heats of fusion and vaporization of HMX.

Approximate BDP Composite Propellant (Multiple-Flame) Model

The BDP multiple flame model for AP composite propellants is another model requiring numerical solution for the burning rate.[20] Baker derived expressions for σ_p from this model, but they are too complicated to be of value in providing any insight.[21] Beckstead succeeded in deriving useful approximate expressions by examining the limiting conditions and magnitudes of terms.[22] At sufficiently low pressures, the combustion is controlled by the diffusion flame between AP and binder and the approximate expression is

$$\sigma_p = \left[\frac{1}{T_F} + \frac{E_{PF}}{RT_F^2}\,\frac{1}{1+(X^*_{PD}/X^*_{PF})}\right] \Big/ \left[1 + \frac{1}{1+(X^*_{PD}/X^*_{PF})}\right] \tag{11}$$

At sufficiently high pressure, the combustion is controlled by the AP monopropellant flame and the approximate expression is the same as Eq. (9). Beckstead took dT_F/dT_0 to be unity in these expressions. Note that there is a shift in the controlling mechanism with increased pressure. A typical low-pressure value calculated from Eq. (11) would be about 0.05%/°C. The high-pressure value calculated from Eq. (9) for the AP flame is about 0.2%/°C. Thus, for the first time, there is a basis for calculating an increase in σ_p with increasing pressure in a composite propellant model. The reason is this shift in the controlling mechanism.

It is apparent from these results that diffusion flame control is less temperature sensitive than AP flame control. This should not be surprising. From a fundamental standpoint, the diffusion process is less temperature sensitive than the kinetics process. The AP flame is a kinetically limited flame. Furthermore, in this particular case, the diffusion flame is more energetic than the AP flame, a fact that will also tend to make the diffusion flame less temperature sensitive. Therefore, diffusion control is a desirable mechanism; this is also true for pressure sensitivity. Within the regime of diffusion flame control, σ_p will decrease with increasing pressure as the diffusion element becomes more dominant. What makes σ_p increase with further increases in pressure is the growing importance of the AP flame.

Summary of Fundamental Mechanisms

Before turning to the parametric results of the more comprehensive models, it is useful to summarize the essence of temperature sensitivity from a fundamental standpoint.

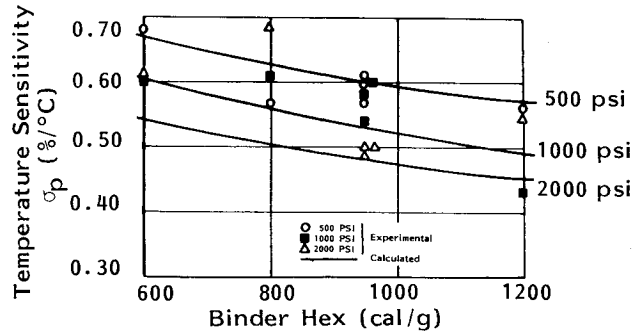

Fig. 4 Calculated σ_p for XLDB energetic binders as a function of heat of explosion and pressure.[13]

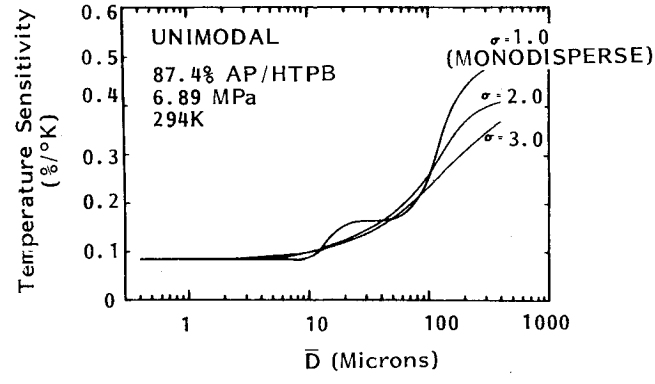

Fig. 5 Calculated σ_p for an AP/HTPB propellant as a function of AP particle size (PEM model).[25]

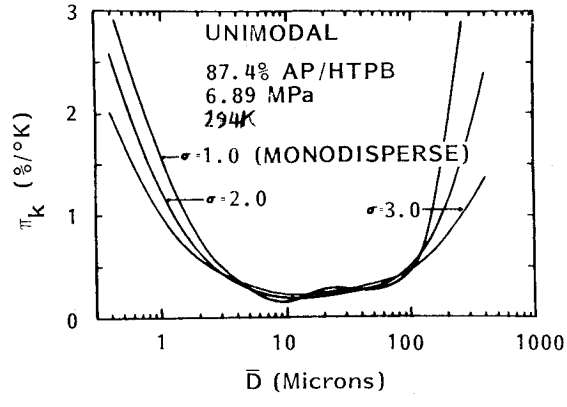

Fig. 6 Calculated $\pi_{p/r}$ for an AP/HTPB propellant as a function of AP particle size (PEM model).[25]

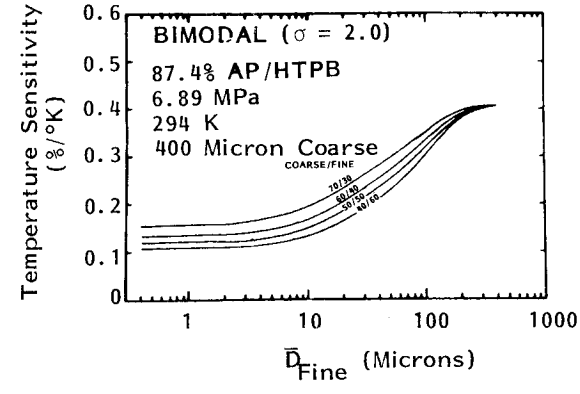

Fig. 7 Calculated σ_p of bimodal propellants as a function of fine size and coarse/fine ratio (PEM model).[25]

With regard to condensed-phase mechanisms, low σ_p is promoted by high T_s because the solid-phase energy content is proportionately less sensitive to T_0 and by an endothermic Q_s because the surface energy balance is proportionately less sensitive to T_0. With regard to gas-phase mechanisms, low σ_p is promoted by high T_F because the heat feedback potential is proportionately less sensitive to T_0, low dT_F/dT_0 because the gas temperature is less sensitive to T_0, low E_g because the reaction kinetics become less sensitive to T_0, and diffusion control because it is less temperature sensitive than the kinetics.

With regard to ingredients, nitramines appear to be beneficial because of their relatively high T_s, endothermic gasification, higher controlling flame temperature than AP, and relatively low dT_F/dT_0. Energetic binders appear detrimental because of the relatively low T_s and exothermic gasification. AP composite propellants can have low temperature sensitivity because of diffusion flame control and a high controlling flame temperature, but not when there is AP flame control because it is a relatively low-temperature kinetically-limited flame with relatively high dT_F/dT_0.

The effects of pressure and temperature on σ_p will depend upon a number of factors. Increases in T_s, T_F, and the reaction rates with increasing pressure will tend to reduce σ_p, but changes in the controlling mechanism and increasing Q_s exothermicity can tend to increase σ_p. It is explicit in the simple models that σ_p will increase with T_0, but that can be counteracted by increases in T_s and T_F and by favorable changes in Q_s and in the composite propellant multiple-flame structure. Thus, it is not surprising that there are no clear systematic trends in data.

Composite Propellant Model Results

BDP Model Results

Calculations with the original BDP model showed a decrease in σ_p with increasing AP concentration, decreasing AP particle size, and decreasing pressure.[21] Each of these trends promotes diffusion flame control. Decreasing particle size and increasing concentration also promote higher burn rates and surface temperatures. Increasing the AP concentration also promotes higher flame temperatures.

Condon, Renie, and Osborn[23] compared various features of their PEM model with the BDP model. The temperature sensitivity results were in basic agreement, differing by a small amount in magnitude. It was also confirmed that the approximate BDP model expressions for σ_p are indeed good approximations at very high and very low pressures.[24] The general pressure effect seen in data for an AP/PBAN propellant was predicted by the models, but the quantitative agreement was not very good.

PEM and Beckstead Model Results for Effects of AP Size Distribution

Renie, Condon, and Osborn[25] and Beckstead[22] published their calculated results showing the effects of AP particle size on σ_p and π_k (actually $\sigma_p/(1-n)$, or $\pi_{p/r}$). Unfortunately, all of the results are at one AP concentration and one pressure, conforming to a standard set of data.

PEM model results for σ_p are shown in Fig. 5. Values of σ_p increase with particle size. The undulations in the monodisperse curve reflect the changing multiple-flame structure as the single particle size increases. The polydisperse curves tend to smooth these out. Increasing σ refers to a widening of the monomodal size distribution. It is evident that sometimes the coarser sizes about the mean are more influential and sometimes the finer sizes are more influential. The increase with particle size reflects the growing importance of the AP flame. PEM model results for $\pi_{p/r}$ are shown in Fig. 6. The high values with very fine sizes are due to the high-pressure exponents calculated for very fine sizes. The high values with coarse sizes are due to both high σ_p and high exponent.

PEM model results for the σ_p of bimodal propellants are shown in Fig. 7. It is observed that σ_p increases with the coarse/fine ratio. Note that the model is not predicting high σ_p for wide-distribution propellants (small fine size combined with the large coarse size). The inability of all of the models to predict the combustion behavior of wide-distribution propellants is well documented.[26,27] The current thinking is that the fine particles in such propellants operate in a very fuel-rich environment. The corresponding low flame temperature would enable the fine-size component to contribute to a high σ_p. The extent of this fuel richness would decrease as the distribution narrows. The corresponding $\pi_{p/r}$ results are shown in Fig. 8. It is observed that $\pi_{p/r}$ also increases with the coarse/fine ratio. Here, the model is correctly predicting high $\pi_{p/r}$ for wide-distribution propellants. However, it is for the reason that the pressure exponent becomes high— which does not properly reflect the correct reason. Beckstead's[28] calculations under the same conditions are very similar. The optimum fine particle size of about 20 μm also corresponds to that for minimum exponent. For these conditions, the best features of diffusion flame control come to bear with the 20 μm size.

Beckstead also used his model to point out a propellant development problem that is qualitatively consistent with experience. He cross plotted the calculated $\pi_{p/r}$ vs the calculated burning rate and distinguished between wide- and narrow-distribution propellants. This cross plot is shown in Fig. 9. The main point is that propellants with low and high burn rates will tend to have higher $\pi_{p/r}$ than those with intermediate burn rates. In the case of the low-burn-rate propellants, it is

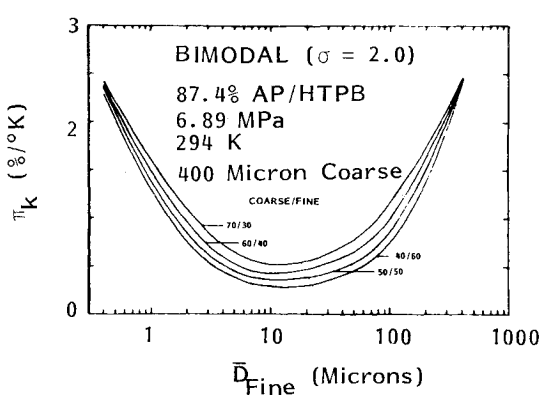

Fig. 8 Calculated $\pi_{p/r}$ of biomodal propellants as a function of fine size and coarse/fine ratio (PEM model).[25]

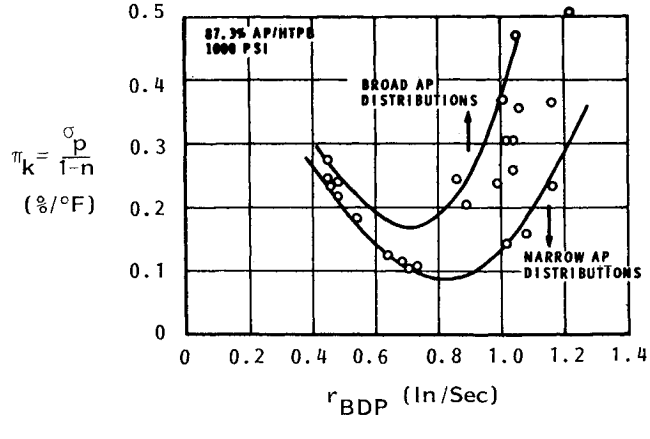

Fig. 9 Calculated $\pi_{p/r}$ of bimodal propellants as a function of calculated burning rate (Beckstead model).[22]

mainly a consequence of higher σ_p. In the case of the high-burn-rate propellants, it is primarily a consequence of the higher pressure exponent. The use of very fine AP to achieve a high burn rate brings about the high exponent because the diffusion flame becomes dominated by the reaction kinetics element (diffusion times become relatively small). Wide-distribution propellants will tend to have higher $\pi_{p/r}$ than narrow-distribution propellants but, as indicated earlier, this prediction is not entirely for the correct reasons. Beckstead's comparisons of calculated and experimental values of σ_p are shown in Fig. 10. The predictions are good for the narrow-distribution propellants. The three cases further from the line are wide-distribution propellants.

Unpublished parametric results of the Cohen-Strand model[27] calculations, in which the pressure and solids loading as well as particle size were varied, are summarized as follows. The σ_p value generally decreases with increasing AP content, decreasing pressure, and decreasing particle size. However, there are exceptions within the various regimes of these variables. This model is in agreement with the other models in that the optimum particle size to minimize $\pi_{p/r}$ occurs at about 20 μm for AP/HTPB at 87% solids and 6.8 MPa. More extensive calculations show that this optimum particle size decreases with increasing pressure and AP content. At the solids loadings of interest, the largest values of σ_p occur at combinations of high pressure and coarse AP; the lowest values of σ_p occur with the finer AP sizes.

Effects of Erosive Burning

It is instructive to first examine the influence of the motor environment by means of the simplifed model. Breaking the heat feedback into a combustion zone component dependent upon T_0 and an external component that is relatively independent of T_0, Eq. (1) becomes

$$\rho_p c_p r(T_s - T_0) - \rho_p r Q_s = \Phi_{\text{comb}} + \Phi_{\text{ext}} \tag{12}$$

Differentiation yields

$$\sigma_p = \frac{1}{T_s - T_0 - (Q_s/c_p)} + \frac{d\Phi_{\text{comb}}/dT_0}{\Phi_{\text{comb}} + \Phi_{\text{ext}}} \tag{13}$$

Thus, σ_p will tend to be reduced by the presence of a fixed external heat source. This can be a radiative or convective source. Erosive burning is in the nature of a convective heating effect.

The PEM model contains an erosive burning analysis in which the crossflow increases the transport properties in the gas phase.[29] The effects on σ_p and $\pi_{p/r}$ were calculated by Renie, Barger, and Osborn.[30] The σ_p results are reproduced in Fig. 11. The essential result is that cross flow reduces the temperature sensitivity in propellants containing coarser AP particle sizes. Finer particle sizes are unaffected because the flame dimensions are well inside the boundary layer and the base burning rates (blowing effect) are high; in other words, the erosive threshold is not exceeded in the finer sizes. With the coarser sizes, σ_p reduction comes about because of the increased heat feedback and surface temperature and because the cross flow tends to shift the competing flame situation in the direction of diffusion flame control. Cross flow tends to increase pressure exponent, but the net effect is a reduction in $\pi_{p/r}$.[30] Unpublished calculations by King and by Cohen and Strand are in essential agreement with these results. Cohen and Strand also calculate that the temperature sensitivity reduction is largest at higher pressures and lower solids loading.

Effects of Aluminum

The Beckstead, PEM,[31] and Cohen-Strand models contain representations of the effects of aluminum on propellant combustion. Only Renie and Osborn have published temperature sensitivity results.[32] In their model, aluminum acts as a heat sink at the propellant surface to the extent that it melts and absorbs its heat of fusion, as well as a heat source in the gas to the extent that it ignites and burns sufficiently close to the propellant to affect the heat feedback. Aluminum agglomeration was not treated in the PEM model at the time.

The effects of the aluminum content (at constant AP/binder ratio) on σ_p are shown in Fig. 12. With fine AP, the aluminum addition is calculated to increase σ_p slightly, which results from the heat sink effect. As shown in Fig. 13, aluminum is not contributing as a heat source with fine-particle AP. On the other hand, with coarse AP, aluminum

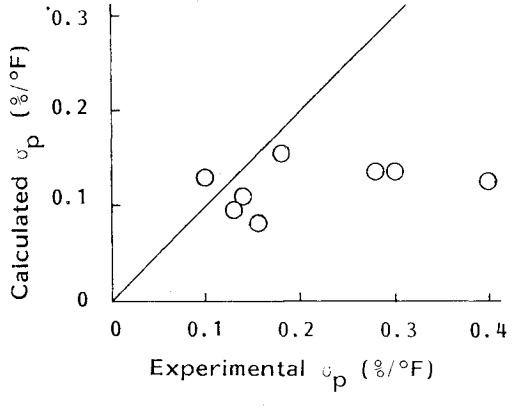

Fig. 10 Comparison of calculated and experimental values of σ_p for AP/HTPB propellants, varying particle sizes (Beckstead model).[28]

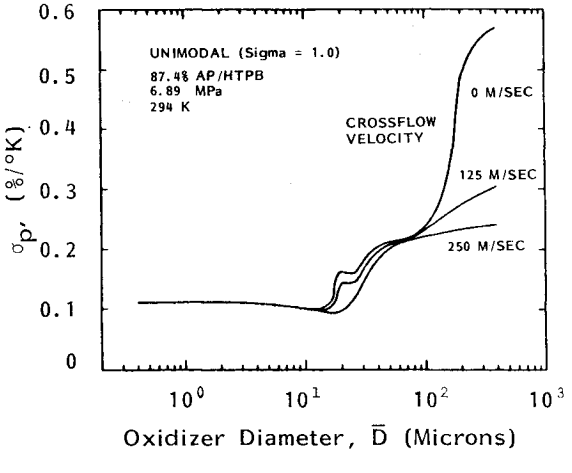

Fig. 11 Effect of cross flow on σ_p as a function of AP particle size (PEM model).[30]

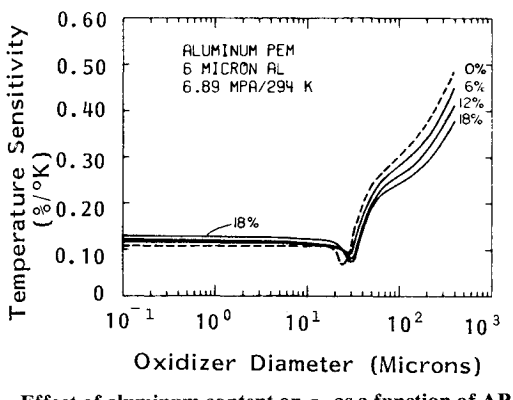

Fig. 12 Effect of aluminum content on σ_p as a function of AP particle size (PEM model).[32]

combustion is a contributing heat source to some extent which has the effect of reducing σ_p. The effect is not large, however. Thus, the effect of aluminum depends upon the AP particle size, which is generally correct, but the models are not able to predict the wide-distribution propellant behavior. The effect of varying the coarse/fine ratio was not calculated, but would probably look like Fig. 7 rather than show the peak σ_p seen in data. The effect of replacing AP with aluminum, such that the AP/binder ratio decreases, was not calculated. However, from the nature of the models, it would be expected that σ_p would increase because the diffusion flame temperature, burning rate, and surface temperature would all decrease.

The calculated effects of aluminum particle size on σ_p are shown in Fig. 14. With fine AP, the heat sink effect depends upon the extent of the aluminum melting at the propellant surface. Since the finer aluminum is more readily melted, σ_p increases with decreasing aluminum size. With coarse AP, the heat source effect depends upon the ease of ignition and combustion of unagglomerated aluminum particles. Since finer aluminum ignites and burns more readily, σ_p now decreases with the decreasing aluminum size. This appears to be the prevalent effect seen in data. However, these calculated effects are not large.

It is interesting to speculate on the effects of aluminum agglomeration. Agglomeration would increase the effective aluminum particle size in the gas. This would reduce the heat source effect and thereby extend the regime in which the aluminum increases σ_p to the coarser AP sizes and finer aluminum sizes. Coarser aluminum might be preferred because, although larger to start with, there would be less melting and agglomeration. The ideal situation would be fine aluminum in low-agglomeration situations: finer AP in narrower AP size distributions and higher burn rate propellants.

Nitramine Composite Propellants

Beckstead and McCarty introduced additional considerations in the model they developed for nitramine composite propellants.[33] Based on their experimental observations, they concluded that there was no statistical average propellant surface (in the BDP model sense) during the combustion of this type of propellant. This led to a time-averaged approach in which various sequential processes were calculated and summed to achieve the aggregate propellant burn rate. This approach can also be applied to AP composite propellants, as first suggested by King[34] and as Beckstead has done in his most recent work.[28] However, Cohen pointed out that there is little difference between the statistical-averaged surface area and the time-averaged approaches when applied to AP composite propellants.[27] The need for a time-averaged approach in modeling nitramine propellants has been disputed.[35]

The relative importance of the various processes in the Beckstead and McCarty model is shown as a function of HMX particle size in Fig. 15. For very fine sizes, the regression rates of HMX and binder control the overall propellant rate. The other two processes are the HMX and binder delay times. Under these conditions, the same basic factors discussed previously would control the temperature sensitivity and the surface-averaged approach would then be in good agreement with the time-averaged one. For very coarse sizes, however, it is calculated that the delay times dominate the combustion. The importance of HMX ignition delay has been disputed[35] and the fact that the HMX regression rate will dominate the combustion of coarse HMX propellants at somewhat higher pressures needs to be resolved.

Calculated temperature sensitivities are compared with experimental data in Fig. 16. Good agreement can be seen, especially in the low-temperature range. The values of σ_p for HMX/HTPB propellants are comparable to those for AP/HTPB propellants. Many compensating factors are involved. Perhaps the most important factors tending to favor the HMX/HTPB propellants are a higher calculated surface temperature, higher oxidizer monopropellant flame temperature, and lower dT_{ox}/dT_0. The ones favoring AP/HTPB propellants are a higher diffusion flame temperature and shorter ignition delay.

CMDB Propellant Model Results

Beckstead CMXLDB Model

Beckstead combined elements of his XLDB and composite propellant models to develop a combustion model for composite-modified XLDB propellant.[36] A comparison of the calculated and experimental values of σ_p for HMX/XLDB propellants is shown in Fig. 17. The model is in fairly good agreement with the low-temperature data and correctly predicts the general trend with varying binder heat of explosion, but the effect of temperature and the overall temperature sensitivity data are not well predicted. It appears that the model is not adequately reflecting the ability of HMX to lower

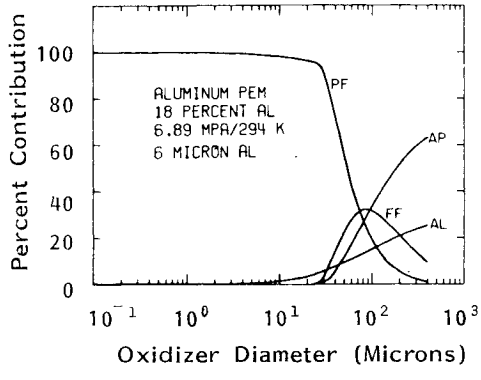

Fig. 13 Calculated percent contributions of the flames to the heat feedback as a function of AP particle size (aluminized PEM model).[32]

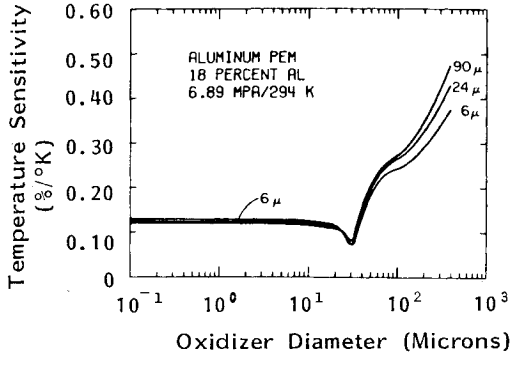

Fig. 14 Effect of aluminum particle size on σ_p as a function of AP particle size (PEM model).[32]

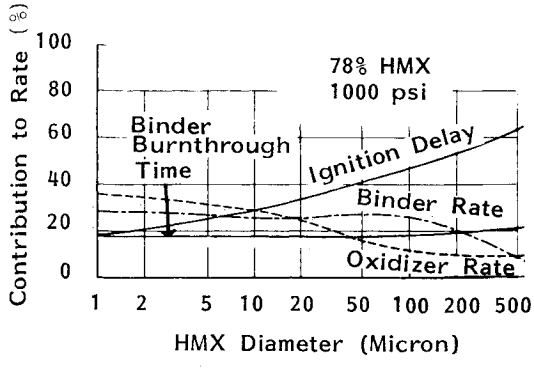

Fig. 15 Percent contributions of various processes to the burning rate of HMX/HTPB propellants (Beckstead and McCarty model).[33]

the temperature sensitivity, perhaps because of the exothermic Q_s and ignition delay of HMX used in the model. To the extent that the calculated values in Fig. 17 are a bit less than those in Fig. 4, it is probably due to the increased surface and gas temperatures resulting from the HMX addition.

Kubota CMDB Models

Kubota and Masamoto developed models for the combustion of CMDB propellants as modifications of the original Kubota double-base propellant combustion model.[37] Both AP- and HMX-filled double-base propellants were treated. Swaminathan and Soosai used these models to perform a parametric study of temperature sensitivity.[38] The models are not as comprehensive as other models for this family of propellants and it was possible to derive closed-form expressions for σ_p. The result for AP/CMDB propellant was

$$\sigma_p = \left\{\frac{r}{r_{DB}}(1-\zeta)\left[\left(\frac{E_g}{RT_F^2}-\frac{2}{T_F}\right)\left(T_s-T_0-\frac{Q_s}{c_p}\right)+1\right]\right\}_F \div \left\{2\left(T_s-T_0-\frac{Q_s}{c_p}\right)+\frac{RT_s^2}{E_s}\right\} \quad (14)$$

and for HMX/CMDB propellant

$$\sigma_p = \left[\left(\frac{E_g}{RT_F^2}-\frac{2}{T_F}\right)\left(T_s-T_0-\frac{\bar{Q}_s}{c_p}\right)+1\right] \div \left[2\left(T_s-T_0-\frac{\bar{Q}_s}{c_p}\right)+\frac{RT_s^2}{E_s}\right] \quad (15)$$

The expressions differ because of the theory that the AP and the region immediately adjacent to the AP burn by a different mechanism from the binder, whereas HMX and the binder burn by the same basic mechanism. The calculated effect of HMX content is shown in Fig. 18. The benefits of the solids loading are largely due to the increased surface temperatures and decreased effective values of exothermic Q_s. There were no comparisons with data, but the predicted effect of the HMX addition appears to be too small—probably because the Q_s value chosen for HMX was not sufficiently different from that of the binder.

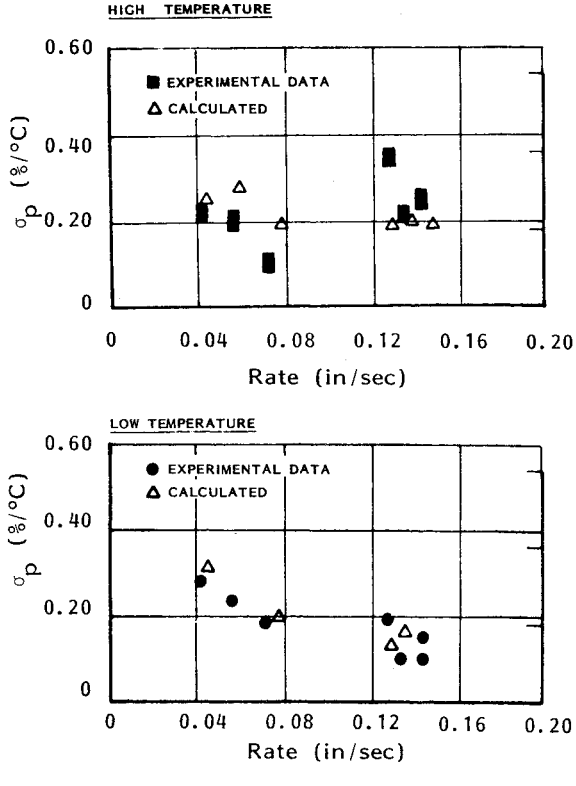

Fig. 16 Comparison of calculated and experimental values of σ_p for HMX/HTPB propellants, various formulations (Beckstead and McCarty model).[33]

Summary of Parametric Results

For AP composite propellants, temperature sensitivity is strongly affected by shifting multiple flame structure. This causes σ_p to generally decrease with increasing AP content, decreasing pressure, and as the size distribution tends toward finer sizes. The major deficiency of the models is their inability to predict the σ_p trends of wide-distribution propellants. By a fortuity they are able to forecast the high $\pi_{p/r}$ of the wide-distribution propellants.

There is predicted to be an optimum range of intermediate particle sizes of AP, associable with a range of intermediate burning rates at which the pressure exponent and $\pi_{p/r}$ become minimal. The minimum n and $\pi_{p/r}$ decrease as the size distribution narrows.

At constant AP/binder ratios, aluminum has a small effect on σ_p of propellants that behave as narrow-distribution propellants. Although not yet proved by calculations, the models would probably show the increase in σ_p when the aluminum substitutes for AP but not the peak in σ_p when varying the coarse/fine AP ratio. There is calculated to be a small net benefit in using finer aluminum and, by inference, metals that ignite and burn more readily than aluminum.

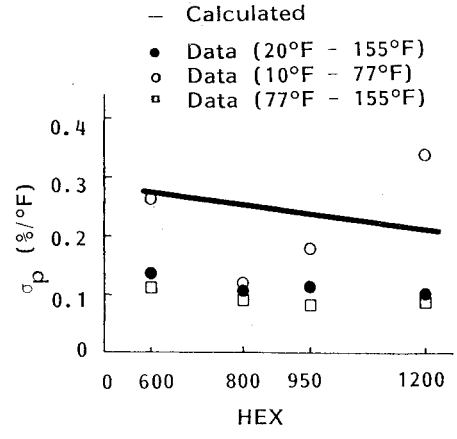

Fig. 17 Comparison of calculated and experimental values of σ_p for HMX/XLDB propellants, various formulations (Beckstead model).[36]

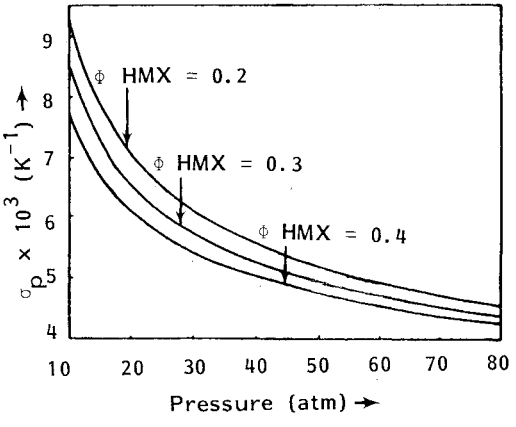

Fig. 18 Effect of HMX content and pressure on σ_p of CMDB propellants.[38]

Predictions that HMX addition to energetic binders reduces σ_p are qualitatively correct, but the predicted magnitudes of this effect are too small. HMX/HTPB propellants are correctly predicted to have σ_p values comparable to AP/HTPB propellants. For CMDB-type propellants, σ_p is calculated to decrease with increasing pressure. For AP composite propellants, it is generally calculated to increase with pressure.

σ_p is generally calculated to decrease with increasing temperature, but the magnitude of this effect is smaller than often seen in data. Erosive burning tends to reduce temperature sensitivity, in particular with propellants containing coarse AP.

Conclusions

Fundamental combustion analysis provides considerable insight into the mechanisms controlling temperature sensitivity and is able to explain many of the major effects seen in experimental data. Basically, the more heat that is stored in the solid and released in the controlling gas-phase reaction, the less their dependencies on temperature and the lower the σ_p.

Comprehensive combustion models are able to give content and meaning to the fundamental aspects of temperature sensitivity in a propellant formulation context. There have not been many direct comparisons of model calculations and σ_p data. Whether or not there should be depends upon one's view of the intents and purposes of analytical models. To the extent that comparisons have been made, it appears that the main deficiencies of the models are their inability to predict trends observed in wide-distribution AP propellants and in the questionable choice of values for some combustion constants. There have been some good predictions and major trends appear to be correct with the foregoing exception.

The combustion models do not treat many aspects of nonideal combustion behavior that could be important and do not treat additives per se in a direct manner. Nonideal behavior is difficult to model because it is less tractable and there are too many unknowns. The models can deal with additives in a useful manner by interpreting changes in the combustion process rather than attempt a priori prediction. An important purpose of the modeling work is to stimulate ideas. Recommendations would include accounting for the temperature dependence of thermal properties and studying effects of binder type.

Acknowledgments

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