

Work-Principle Model for Predicting Toxic Fumes of Nonideal Explosives

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Abstract

The work-principle from thermodynamics was used to formulate a model for predicting toxic fumes from mining explosives in underground chamber tests, where rapid turbulent combustion within the surrounding air noticeably changes the resulting concentrations. Two model constants were required to help characterize the reaction zone undergoing rapid chemical transformations in conjunction with heat transfer and work output: a stoichiometry mixing fraction and a reaction-quenching temperature. Rudimentary theory with an unsteady uniform concentration gradient was taken to characterize the combustion zone, yielding 75% for the mixing fraction. Four quenching temperature trends were resolved and compared to test results of ammonium nitrate compositions with different fuel-oil percentages (ANFO). The quenching temperature 2345 K was the optimum choice for fitting the two major components of fume toxicity: carbon monoxide (CO) and total nitrogen oxides (NO_x). The resulting two-constant model was used to generate comparisons for test results of ANFO compositions with additives. Though respectable fits were usually found, charge formulations which reacted weakly could not be resolved numerically. The work-principle model yields toxic concentrations for a range of charge formulations, making it a useful tool for investigating the potential hazard of released fumes and reducing the risk of unwanted incidents.

Keywords: Toxicity, Fumes, Nonideal Explosives

1 Introduction

The mining explosives tested in the underground chamber generate reaction zones that undergo turbulent mixing and rapid combustion with the chamber air, further transforming the fume concentrations, unlike rock blasting where the late-stage burning is inhibited. The NIOSH underground test chamber is 274 m³, holding 324 kg air at standard conditions. Galvanized tubing or steel pipe is used to retain the 4540 g of mining explosive under test. The total charge mass, nominally 4712 g, includes a 172 g booster with 50–50 weight percent TNT and PETN. The resulting fume toxicity is normally dominated by carbon monoxide CO and total nitrogen oxides NO_x, taken as the sum of nitric oxide (NO) and nitrogen dioxide (NO₂). The traditional Russian formula for the relative fume toxicity (RFT) is their weighted sum: $RFT = CO + 6.5 \cdot NO_x$ [1, 2].

Traditional detonation codes are unable to account for the unfinished or transformed reactions with air ingestion, without notable and questionable modifications. Test results for CO and NO_x could not be reconciled with the theoretical predictions by detonation codes that rest just upon the traditional requirements of the Zeldovich-von Neumann-Doering (ZND) theory [3, 4]. For ZND theory, the reaction thermicity disappears at the Chapman Jouguet (CJ) condition to remove a numerical singularity in the related flow equation. The requirement of zero-thermicity is a recognized conflict for nonideal explosives that undergo uninterrupted transitions from detonation to deflagration [5]. The conflict can be rendered moot by postulating some type of loss term (degradation) that effectively removes the CJ singularity [6]. ZND theory requires a real-gas equation-of-state (EOS) [7] for the isentropic trajectory from the CJ regime to some quenching temperature(s), whereupon the relevant fume concentrations are regarded as frozen. For the underground tests, the turbulent mixing and rapid combustion are not isentropic processes. Rather than postulating a questionable rendition of ZND theory with a non-isentropic trajectory and a requisite loss term, a different theoretical platform was chosen.

The work-principle from traditional thermodynamics with imposed constraints was utilized to render a computational algorithm for predicting toxic fumes for a wide range of explosive formulations. The work-principle capitalizes on the restorative influences that constantly try to render total thermodynamic equilibrium, diminishing the role of process history. Though the model has theoretical disadvantages when compared to the rigorous structure of detonation theory, there are issues worth noting: First, the whole thermodynamic trajectory for the nonideal process is not required, just that for the region near the quenching transition. Utilizing a real-gas EOS, which is itself a questionable issue, is unnecessary, as the renowned ideal form suffices. Second, the work-principle model incorporates a loss term, which is ultimately determined rather than stipulated. Third, the thermodynamic trajectory found for the quenching state is normally nonisentropic, revealing the irreversible consequences of turbulent mixing, rapid combustion and other reaction-zone losses.

This report discusses the work-principle technique, the Z-state constraint for the reaction-fume zone without interaction and the N-state constraint for reckoning loss. The rudimentary mixing rule with its 75% fraction and the trials that yield the optimum quenching temperature are reviewed. The graph of the loss rate versus fuel percent, which resembles a ranking trend for the charge performance, is worth noting. Lastly, the two-constant model is used to generate comparisons for test results of ANFO compositions with additives.

2 Reaction Process in Work-Principle Terms

The work-principle technique recasts the second law of thermodynamics for a composite system, which is isolated from the rest of the universe and therefore governed by the four laws of thermodynamics [8, 9]. The work-principle construction retains thermodynamic interaction in restricted internal ways for its three components: the working fluid, the reservoir and the mechanical agent. The working fluid transfers heat or works upon the reservoir in reversible or irreversible ways. It works reversibly upon the mechanical agent in other ways (non-expansion). No mass transfer occurs, so the working fluid retains constant mass while undergoing reaction or transformation. The working-fluid is regarded as restored or wound-up thermodynamically to the wanted (or initial) state within the isolated composite system via reversible work, rendered by the mechanical agent.

The work-principle model for toxic fumes takes the zone of transforming reactants as the working-fluid, their surroundings as the reservoir and the mechanical agent ultimately remains nondescript. The working-fluid is originally composed of the explosive ingredients with a tiny (or zero) quantity of chamber air, called reactant-air to distinguish it from the remaining portion taken as a reservoir component. Reactant-air is not a nebulous quantity, but rather the proportion tabulated in the thermodynamic reaction code (TDRC). The rupture and fragmentation of the cylinder pipe or tube is not wholly ignored, though it is reckoned with rather indirectly through the loss term in the work-principle model.

Restoring influences continually try to maintain mechanical, thermal, and chemical equilibrium within the reaction zone. For an underground test, the zone expands rapidly, the temperature drops quickly and the reaction rates fall precipitously, so the chemical equilibrium falters, resulting in non-equilibrium concentrations. Wall or dust interactions or transformations those remain noticeable over the hour of measurement ruin the notion of wholly frozen concentrations. The rusty-tinted oxidation that rapidly transforms NO into NO₂ at cooler temperatures conserves the NO_x, which is lost more slowly otherwise. Concentrations that remain useful for toxic fume comparisons stay relatively unchanged from the quenched state, like CO and NO_x, rather than NO or NO₂.

The reservoir conditions are taken equal to the standards utilized for reducing the underground test data: temper-

ature $T_R = 298.15$ K (25 °C) and pressure $P_R = 101325$ Pa (1 atmosphere). The work-principle is more utilitarian when the reservoir retains those constant characteristics, implying that it has tremendous mass compared to the other two components. This restriction is compatible with the underground test circumstances, where the working fluid consists of the total charge, ~4.7 kg, plus the reactant-air, with typically less mass. The resultant mass is tiny compared to the reservoir mass which includes the remaining chamber air, roughly 320 kg, without worrying about the walls or other inert objects that help sustain the reservoir conditions. With the restriction of constant reservoir conditions, the differential work principle can be rendered in integrated form with a useful quasi-potential.

3 Working-Fluid State Function Notation

Throughout the report, the zone-summing (or explicit) variables are taken per unit constant mass of the working fluid, which is the type of data used with the TDRC. Reduction in the notation is convenient for rendering imposed constraints. The resultant sum of chemical potentials μ_K 's times their respective stoichiometry coefficients ν_K 's yields Q , which works with the reaction coordinate Z . The reciprocal of the molecular weight A , the sum of N_K , resets the units, while the negation (minus) means that Q normally has the sign of Z (i.e., spontaneous reaction in an insulated rigid box). The flow work W , or ratio of pressure P to density ρ , works with the natural logarithmic density $Y = \ln[\rho/RHO]$, where RHO is just a units constant. The traditional differential relation for the internal energy U is rewritten in contracted form, relation (1). The notation δ or d means infinitesimal variation or differential respectively, while Δ implies non-infinitesimal change.

$$dU = T \cdot dS - P \cdot d(1/\rho) + \sum_K \mu_K \cdot dN_K$$

$$W \equiv P/\rho$$

$$Y \equiv \ln(\rho/RHO)$$

$$RHO = Const$$

$$Q \equiv -N \cdot \sum_K \mu_K \cdot \nu_K$$

$$dZ \equiv \frac{dN_K}{N \cdot \nu_K}$$

$$N \equiv \sum_K N_K$$

$$dU = T \cdot dS + W \cdot dY - Q \cdot dZ \quad (1)$$

Real-gas EOS usually reduce to the Grüneisen form, $W = J \cdot (U - I)$, where W is proportional to U with coefficient functions J and I that remain roughly constant over a modest

thermodynamic domain. Working-fluid state functions W and T remain positive for stable fluids [8], while Q can undergo sign reversal. The third law of thermodynamics stipulates that zero temperature is unattainable, so T and T_R are never regarded as zero [10]. There are two ways to nullify the chemical-work $[Q, Z]$ term: the restriction to constant Z , which yields frozen concentrations or the restriction to (constant) zero Q , which implies chemical equilibrium.

$$\Psi \equiv U - T_R \cdot S + P_R/\rho, T_R, P_R \text{ remain constant} \quad (2)$$

The quasi-potential Ψ in definition (2) incorporates the working-fluid properties U , ρ , and entropy S per unit working-fluid mass in conjunction with two constant reservoir properties T_R and P_R . Rigorously speaking, the retention of the reservoir influence means that Ψ is not a thermodynamic state function [11], though it retains the zone-summing character of the working-fluid state functions. This renders Ψ with a formidable nature that is quantifiable throughout the whole of thermodynamic space, regardless of the process undertaken or imagined.

4 Theory Underlying the Work-Principle

The work-principle theorem with the restriction to constant reservoir conditions is succinctly stated in relation (3), using the Ψ -definition (2). The rule requires that the resultant for the work done upon the mechanical agent, $WORK$, plus the quasi-potential change, $\Delta\Psi$, remain zero for reversible processes or negative for irreversible processes [8, 9]. For reversible processes, the $WORK$ done upon the mechanical agent would equal (=) the reduction in the quasi-potential, $[-(\Delta\Psi)]$. Natural processes refer to recognizable (non-infinitesimal) changes or jumps in thermodynamic variables over (finite) time, so they are irreversible, however slight, and the inequality ($<$) holds. Reversible transformations with their innumerable quasi-static steps would take forever to render such a transition, though they represent the unreachable limit.

$$WORK + \Delta\Psi \leq 0 \quad (3)$$

For natural closed-cycle processes, the working-fluid returns to its original state, restoring the quasi-potential, $\Delta\Psi = 0$, so reversible work must be rendered by (not upon) the mechanical agent, $WORK < 0$. The $WORK$ inequality would occur on every cycle, without the reverse possibility, removing any prospect of perpetual motion (2nd kind), regardless of the thermodynamic process undertaken.

In the non-cyclic rendition for modeling fumes, the working-fluid is taken to the wanted (initial) reactant state, where the mechanical agent is rendered moot, so it is unnecessary to identify it with some underground object. With $WORK = 0$, the work-principle formula (3) reduces to $\Delta\Psi \leq 0$. Without restoration work, Ψ is unable to increase, though it decreases from natural fluctuations until it reaches a trapping minimum condition. Without some constraint,

the working-fluid ultimately reaches the reservoir circumstance, yielding no information regarding the route taken. The notion of removing and imposing hypothetical constraints, to tentatively stall the trajectory descent at intermediate circumstances (key-states), circumvents the no-information trap and represents a way to characterize the wanted process.

5 Resolution of the Z-State and N-State Constraint

The work-principle model for resolving toxic fumes imposes just two constraints upon the reaction zone: the zero-loss constraint for the Z-state and the nonzero-loss constraint for the rate-quenching N-state. The notation $X = \text{constant}$ represents a generic thermodynamic constraint upon some function of working-fluid variables. The technique requires an unrestrained variable, taken as the logarithmic density Y , since the rigid-box condition, $Y = \text{constant}$, is not required. The TDRC yields circumstances for chemical equilibrium rather than frozen concentrations, so $Q = \text{zero} = \text{constant}$ rather than $Z = \text{constant}$. For manipulating constraint relations, the working-fluid state variables are regarded as functions of $[X, Y, Q]$ rather than $[S, Y, Z]$. Relations (1) are worthwhile for rearranging terms. For the quasi-potential minimum, the thermodynamic trajectory is tangent to the constraint surface, so δX , Q , δQ terms disappear, while the unrestrained δY terms remain, yielding the Ψ -minimum for the generic- X constraint, relation (4).

$$\begin{aligned} \delta\Psi &\equiv \delta Y \cdot \left. \frac{\partial\Psi}{\partial Y} \right|_{X,Q} \\ &= \delta U - T_R \cdot \delta S + P_R \cdot \delta \left(\frac{1}{\rho} \right) \\ &= \left(1 - \frac{T_R}{T} \right) \cdot \delta U + \left(\frac{T_R}{T} - \frac{P_R}{P} \right) \cdot W \cdot \delta Y - \left(\frac{T_R}{T} \right) \cdot Q \cdot \delta Z \leq 0 \end{aligned}$$

$$\text{Taking } K \equiv \frac{P}{\mathfrak{R}T}, K_R \equiv \frac{P_R}{\mathfrak{R}T_R}, \alpha_X \equiv \frac{1}{W} \cdot \left. \frac{\partial U}{\partial Y} \right|_{X,Q}$$

$$\delta\Psi|_{Min.} = W \cdot \delta Y \cdot \left[\left(1 - \frac{T_R}{T} \right) \cdot \alpha_X - \frac{T_R}{T} \left(\frac{K_R}{K} - 1 \right) \right] = 0 \quad (4)$$

The K -function definition, where \mathfrak{R} is the Universal Gas Constant, was utilized for restating the terms in Eq. (4). For reservoir conditions, $K = K_R = 40.874 \text{ mol/m}^3$. For zero interaction, the working fluid retains its original internal energy, $X = U = \text{constant} = U_0$, so the loss term disappears, $\alpha_X = \alpha_U = 0$, via its definition. With $W \cdot \delta Y$ nonzero, the residual bracket term reduces to zero upon reaching the minimum, yielding $K_Z = K_R$, where the Z subscript refers to the Z-state. The triplet $[U_Z, K_Z, Q_Z] = [U_0, K_R, 0]$ characterizes the Z-state for any thermodynamic working-fluid, regardless of its EOS representation or structure or composition [12].

The N-state was resolved for nonzero reduction ($-dU$), taken as work output upon or heat transfer to the reservoir, during the expansion ($-dY$), yielding a non-unique though positive loss rate α_X . The N-state constraint was reckoned in log-log $[T, K]$ form, relation (5), by requiring that $[J \cdot \alpha_X]$ remain constant $[J \cdot \alpha_L]$ and integrating the differential equation noted in Appendix A. This restriction was rendered plausible by recognizing that J reduces to the Grüneisen gamma Γ_G function, which remains relatively constant over a modest thermodynamic domain. The N-state constraint relation was taken back though the Z-state to remove the unwanted constant of integration. For the rough approximations utilized in the work-principle technique, the Z-state Γ_G was taken, rather than recursively solving for the $N\text{-}\Gamma_G$ though that is a tractable refinement.

$$\left[\left(1 - \frac{T_R}{T_N} \right) \cdot \alpha_L - \frac{T_R}{T_N} \left(\frac{K_R}{K_N} - 1 \right) \right] = 0$$

$$\ln \left(\frac{T_N}{T_Z} \right) = J \alpha_L \cdot \ln \left(\frac{K_N}{K_Z} \right) \quad (5)$$

where $K_Z = K_R$, $T_N = T_Q$, $J, \alpha_L \approx \text{Const.}$

With T_Z, K_Z and J ($\approx \Gamma_{GZ}$) known, the Ψ -minimum $[T, K]$ bracket and logarithmic $[T, K]$ constraint still contain three unknowns $[K_N, \alpha_L, T_N]$, where the N subscript refers to the N-state. Hypothetically, the N-state represents the last remnant of total thermodynamic equilibrium, where the relevant rates drop precipitously with zone temperature, quenching further transitions and regulating the outcome. The two relations yield solutions with the requirement that the N-state temperature T_N refer to a unique quenching temperature T_Q , which was thought worth trying. Within the work-principle model therefore, the Z and N states were resolved without taking into account the whole thermodynamic trajectory or process history.

6 Thermodynamic Reaction Code, TDRC

Though historically TDRC have utilized rate-kinetic formulations, more recently they use numerical minimization, so two theorems derived from the traditional work-principle are quite renowned, namely the minimizations of Gibbs energy and Helmholtz energy [9]. Restrictions within the TDRC that correspond to the working fluid under thermal and mechanical equilibrium invoke Gibbs minimization. Replacing the mechanical equilibrium with the restriction of constant density therein would invoke Helmholtz minimization. The type of minimization utilized within the TDRC routines is regulated internally by the choices of the TDRC input [13], which were readjusted in a compatible way to resolve the trapping Ψ -minimum under an imposed constraint. The TDRC output for the Ψ -minimum then yields the remaining thermodynamic state functions and concentrations for chemical equilibrium. The Z-state results are utilized for resolving the rate-quenching N-state, where

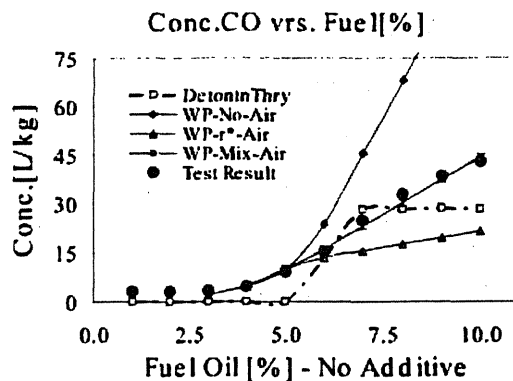


Figure 1. Types of theoretical CO concentration versus fuel percent, with test results.

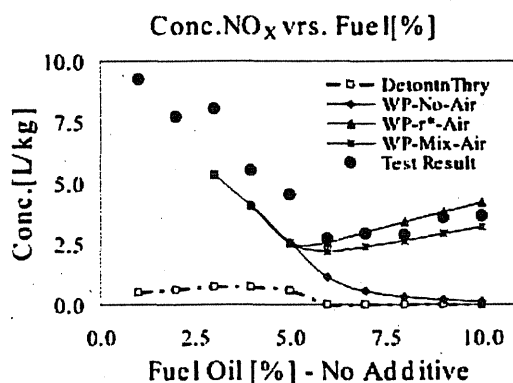


Figure 2. Types of theoretical NO_x concentration versus fuel percent, with test results.

relevant frozen concentrations are comparable to underground fume measurements.

For ZND results without ingested air, the reference code was old [14], so the charge formulations were rerun with updated code and real-gas EOS, without trying to implement non-standard modifications [15]. Work-principle Z or N-state results for typical reactants were rarefied, $K_N < K_Z = K_R$, with high temperature, $T_Z > T_N = T_Q$, and minor proportions of condensed phases. Under such conditions any real-gas EOS rendered in the virial K-series from the virial P-series [7], would reduce to the universal ideal form, because the higher-order terms remain negligible. Logically the thermodynamic circumstances warrant using the NASA Lewis Complex Chemical Equilibrium Code for ideal gases with condensed phases taking up zero volume [16]. Registered ingredients in the TDRC data files were used, when possible. The notable exception was the fuel oil, which had the molecular formula $\text{C}_{14}\text{H}_{24}$ and heat of formation -247 kJ/mol, taken from a regression fit for related hydrocarbons.

The NASA-TDRC has the wonderful installed capacity to resolve the ratio of fuel-to-oxidizer (ROF) mass fractions for stipulated r -equivalence (r^*), a type of common valance. The TDRC yields the ROF for stoichiometry with r^* restricted to unity, which would require 5.68% fuel oil in our ANFO composition, when reactant-air and the booster are ignored.

When the TDRC ingredients without reactant-air yield $r^* > 1$, the TDRC can resolve the requisite proportion for the reduction to $r^* = 1$, referred to as r^* -air. For this trick, the ingredients were tagged 'fuels' regardless of their nature, with reactant-air the only 'oxidizer'. The trick won't work when no-air results yield $r^* \leq 1$, since the requisite quantity of ingested air would be negative or zero, whereupon none is taken.

The CO and NO_x concentration versus fuel percent are shown in Figures 1 and 2, respectively. Theoretical trends are reported for the detonation code with standard runs, work-principle results for no-air, r^* -air, their mixture and the test results (averages) [17]. Concentrations represent the specie volume per unit total charge mass [(L/kg) or (cm³/g)] taken at the stipulated reservoir conditions. To reduce the graphical clutter, only the work-principle results for the optimum (in retrospect) quenching temperature are displayed. The graphs reinforce the modeling problems noted previously: the unmodified detonation code and no-air trends would not fit the test results. Fuel-rich test data were trapped between the r^* -air and no-air trends, indicating that a weighted sum (mixture) should work.

7 Rudimentary Mixing Theory

For the rapid turbulent air combustion, the mixture concentration c_j of the J -th species was taken as a weighted superposition of the TDRC results for $c_j(\text{No})$ without air and $c_j(r^*)$ for r^* -air stoichiometry. The relative proportions depend upon a 'mixing' fraction, which was resolved with the following rudimentary hypothesis. The reaction-fume zone was regarded as spherical, with radius $R = R(t)$, at time t . The centre concentration $c_j(0)$ was taken as $c_j(\text{No})$. The surface concentration $c_j(R)$ was taken as $c_j(r^*)$. The unsteady concentration gradient $k = k(t)$ was regarded as uniform and therefore equal to the concentration difference $[c_j(R) - c_j(0)]$ divided by the radius R . Integration with respect to r over the range, $0 \leq r \leq R$, yields the mixing rule, relation (6): the zone-average concentration $\langle c_j \rangle$ or c_j equals $c_j(\text{No})$ times 25% plus $c_j(r^*)$ times 75%. The 75% is referred to as the mixing fraction, while the other multiplier, 25%, is just the difference from unity (100%). The mixing rule is rendered trivial when r^* -equivalence implies a negative or zero quantity of reactant-air, since $c_j(r^*)$ reduce to $c_j(\text{No})$ results. Replicated tests had sufficient concentration dispersion that refinements in the mixture-rule theory were not warranted [17].

$$c_j \equiv \langle c_j(r) \rangle \equiv \frac{\int_0^R c_j \cdot r^2 \cdot dr}{\int_0^R r^2 \cdot dr} = c_j(0) + \frac{3 \cdot k \cdot R}{4}$$

$$= \frac{c_j(0)}{4} + \frac{3 \cdot c_j(R)}{4} \quad (6)$$

$$\text{where } c_j(r) = c_j(0) + k \cdot r$$

$$\text{from } \frac{\partial c_j(r)}{\partial r} \equiv k = \frac{[c_j(R) - c_j(0)]}{R}$$

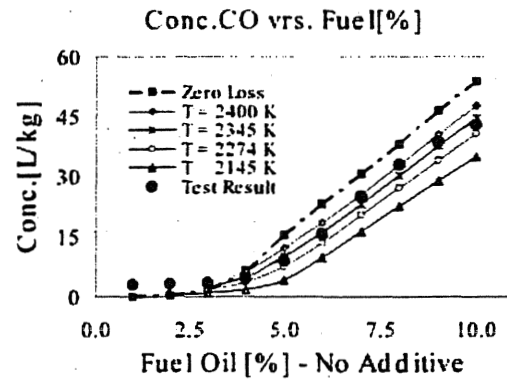


Figure 3. Quenching-temperature CO concentration versus fuel percent, with test results.

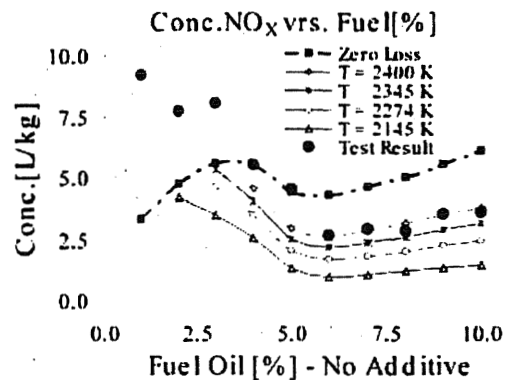


Figure 4. Quenching-temperature NO_x concentration versus fuel percent, with test results.

8 Quenching Temperature Optimum

The mixture-rule CO and NO_x concentrations versus the ANFO fuel percent are shown in Figures 3 and 4, respectively. Theoretical trends were generated for four quenching-temperatures: 2145 K, 2274 K, 2345 K and 2400 K. Normally, comparisons refer to the rich (over 7%) or mid (4% to 7%) fuel range rather than the lean (under 4%) fuel range, where the CO was negligible and the NO_x was hard to fit. For the CO graph, the rich/mid results were in the 2274–2400 K range. For the NO_x graph, the rich results were in the 2345–2400 K range. With the underlying test-data uncertainty and wayward (or no) fits into the lean range, temperature interpolation was regarded as unwarranted, so the quenching optimum was taken as 2345 K.

Unfortunately, the work-principle was unable to predict N-state results for explosives that react weakly (coolly), which is why there are graphical regions without theoretical results. There is no numerical resolution possible when the Z-state temperature T_z is less than the quenching temperature T_Q . It would be wrong to infer that the work-principle, which rests upon the four laws of thermodynamics, or the restrictions of constant reservoir or NO WORK were faulty, rather than the underlying constraints or stipulations used to resolve them. For the unsolved cool circumstances, it

remains unclear whether total thermodynamic equilibrium was unattainable or the last remnant was reached prior to the Z-state, which thereupon would be relegated to the non-equilibrium regime. Refinements that might circumvent or ultimately overcome the tractability issue are noted later.

9 Role of Ingredient Composition for the Loss Rate

For the underground tests, the reaction-zone energy transferred to the retaining fixture, the reservoir air and chamber walls is wasteful, while for rock blasting, it would fragment and heave rocks. The working-fluid's capacity to transfer energy to its surroundings is reckoned from the loss rate α_L , shown plotted against fuel percent in Figure 5. The graph resembles a ranking trend for the charge performance (α_L) versus ingredient composition (fuel-oil), where the result near 6% represents the charge formulation that should render the most work (maximum- α_L).

Generally, the N-state solutions yield positive α_L , under or over unity, thereby revealing that typical trajectories through the quenching temperature T_Q are not isentropic. Relation (7) where $X=S=\text{constant}$ for an isentropic trajectory yields the requirement that $\alpha_X = \alpha_S = 1$, which would occur only rarely (coincidentally). Therefore, the work-principle technique, with its propensity for a non-

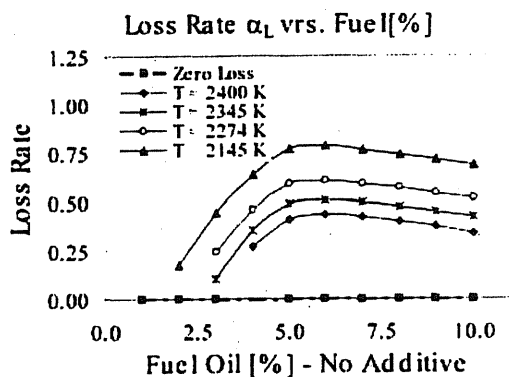


Figure 5. Quenching-temperature loss-rate constant versus fuel percent.

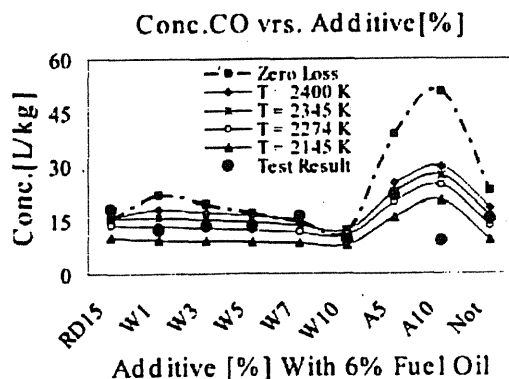


Figure 6. Quenching-temperature CO concentration versus additive percent, with test results.

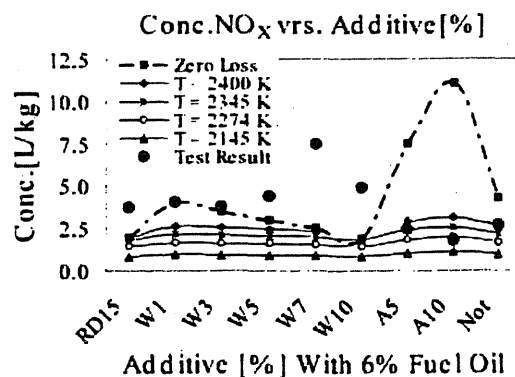


Figure 7. Quenching-temperature NO_x concentration versus additive percent, with test results.

isentropic trajectory, differs notably from the traditional unmodified ZND theory.

$$\alpha_s = \frac{1}{W} \cdot \frac{\partial U}{\partial Y} \Big|_{s,Q=0} = \frac{1}{W} \cdot \frac{\partial U}{\partial Y} \Big|_{s,Z} = \frac{W}{W} = 1 \quad (7)$$

10 Charge Formulation with Additives

The notation used for graphing the results of ANFO with 6% fuel oil and an additive was: RD15 for 15% rock dust, Not for none, W for water and A for aluminum, where the number represents the percentage. The mixture-rule concentrations for CO and NO_x versus the type of additive are shown in Figures 6 and 7, respectively. The CO fits were respectable on the whole, except for A10. The NO_x fits for Not, A5 and A10 were decent, those for RD15, W1, W3 and W5 were marginal, while those for W7 and W10 were poor. Compositions with higher additive percentage might not have reacted completely in the underground tests, contrary to TDRC presumptions, making those comparisons questionable: RD15, W7, W10 and A10. There were no ingredient circumstances for which the TDRC numerical convergence was ruined by too many condensed phases, though it would not be unreasonable to omit condensed phases that are unlikely to form in a rapid explosion.

11 Unresolved Quenching N-States

For rough approximations, universally fixing the loss rate rather than the quenching temperature resolves the tractability issue with cool explosives, though that technique tends to render worse fits to the test results. The resolved N-state trends and NO_x test results in Figure 4 have roughly positive concavity, whereas the wholly tractable zero-loss trend with restricted (zero) constant α_L has a reversing profile with a negative concavity, illustrating wrongful fit. The resolved loss rates for rock-dust/water (aluminum) results in Figure 7 were under (over) 0.5. Were α_L uniformly taken as 0.5 instead, the *unrestricted* N-state temperature

and related NO_x would decrease (increase), universally worsening their fit-discrepancy in Figure 7. The wrong-way changes can be inferred from the correlated information in the multiple-temperature trends of Figures 5 and 7 (or 4). When the resolved loss rate is near 0.5, like the Not result, the choice of restriction is hardly relevant. Though the work-principle technique using the quenching-temperature stipulation remains more tenuous, with residual tractability issues, the resolved trends yield more consistent fits than those from trying to uniquely stipulate the loss rate. The logical recourse for cool explosives would be to improvise constraints that work in the thermodynamic regime denser than the Z-state and study their ramifications.

12 Conclusions and Recommendations

The work-principle model as formulated rests upon relatively few postulates and restrictions with constraints that were tailored for underground chamber tests, not rock blasting. Two requisite model constants were resolved: the 75% mixing fraction from rudimentary theory and the trial-optimum quenching temperature $T_Q = 2345$ K. The quenching optimization refers to fits for the two major components of fume toxicity, CO and NO_x , not other types of reaction products. With the unique quenching temperature, the unstipulated reaction-zone loss rate was resolved, though it was found to depend upon the ingredient composition of the charge formulation. The graphical trend for the loss rate α_L versus some ingredient proportion (fuel oil) was recognized as useful for ranking the work output of the charge formulations, revealing an optimum choice (~6%). The work-principle model would not yield N-state results when the Z-state temperatures were less than the quenching temperature, which occurred for weakly reacting (cool) explosives. Though the tractability issue disappears when the loss rate was uniquely fixed instead of the quenching temperature, the trends have the wrong profile and render inferior fits overall. The two-constant model, originally recommended, has respectable resolving power for predicting toxic release hazards or investigating ingredient changes that could reduce the risks of unwanted fume incidents.

Recommended extensions for the work-principle technique logically include trying to impose constraints that characterize different types of rock blasting or resolve cool explosives in the underground tests. Hypothetically, this would require using a TDRC with a real-gas EOS for the higher density regime, where the internal energy is not wholly regulated by temperature. Though the ingestion of air could remain relevant in the underground case, the rock or stratum would normally inhibit air from reaching the zone of transforming fumes, reducing the modeling difficulty. Non-ideal reaction, requisite loss-rate, non-isentropic trajectory and the retention of total thermodynamic equilibrium will remain issues worth investigating.

13 Appendix A. Rendering Form to the Imposed Constraint

With the work-principle, there is no requirement for the thermodynamic trajectory to 'ride' the imposed constraint representing the wanted process, except in proximity to the trapping minimum of the quasi-potential. The constraint resolution presumes that the real-gas EOS reduces to Grüneisen form in relations (8), with coefficient functions J and I that remain relatively constant over a modest thermodynamic domain, near the Z-state or N-state. The K -function was rewritten in terms of the imperfect function Φ , which represents the real-gas departure from ideality. When Φ reduces to unity and the molecular weight is typical, ~24.47 g/mol, the requirement $K_Z = K_R = 40.874$ mol/m³ yields the rarefied Z-state density, -1 kg/m³.

$$W = J \cdot (U - I), \Phi \equiv \frac{W}{NRT}, K \equiv \frac{P}{RT} = \Phi \rho N \quad (8)$$

The N-state constraint relation was formulated with the logarithmic derivative of temperature T with respect to K at constant X and Q . Reduction in form occurs for the reasonable presumptions that the thermodynamic derivatives of A , Φ , J and I remain negligible in comparison, yielding the $J \cdot \alpha_X$ result in relation (9). Restricting $J \cdot \alpha_X$ to constant $J \cdot \alpha_L$ yields the logarithmic T - K constraint relation (5) by integration. The unwanted X - Q integration constant (function) was removed by tracking the N-state constraint through the Z-state result.

$$\begin{aligned} \frac{\partial[\ln(T)]}{\partial[\ln(K)]} \Big|_{x,Q} &= \frac{\frac{\partial[\ln(T)]}{\partial Y} \Big|_{x,Q}}{\frac{\partial[\ln(K)]}{\partial Y} \Big|_{x,Q}} = \frac{\frac{\partial[\ln(W)]}{\partial Y} \Big|_{x,Q} - \frac{\partial[\ln(N \cdot \Phi)]}{\partial Y} \Big|_{x,Q}}{1 + \frac{\partial[\ln(N \cdot \Phi)]}{\partial Y} \Big|_{x,Q}} \\ &\approx \frac{\partial[\ln(W)]}{\partial Y} \Big|_{x,Q} = \frac{1}{W} \cdot \frac{\partial W}{\partial Y} \Big|_{x,Q} \\ &= \frac{\partial W}{\partial U} \Big|_{x,Q} \cdot \frac{1}{W} \cdot \frac{\partial U}{\partial Y} \Big|_{x,Q} \approx J \cdot \alpha_X \end{aligned} \quad (9)$$

$$\text{Where } \frac{\partial W}{\partial U} \Big|_{x,Q} \approx J \approx \frac{\partial W}{\partial U} \Big|_{\gamma,Z} \equiv \Gamma_G = \frac{1}{T} \cdot \frac{\partial T}{\partial Y} \Big|_{s,Z}$$

Recognizing that the thermodynamic derivatives for J reduce to the Grüneisen gamma function, Γ_G , requires taking the differentiation of the reduced EOS in two ways, noted by the subscript shift. The requirement that the J and I deviations remain negligible was invoked previously. The resolved Z-state Γ_G is utilized for J , rather than the unresolved N-state Γ_G , which requires recursive solutions, though that represents a tractable and worthwhile refinement.

$$\begin{aligned} \Gamma_s &\equiv \frac{c^2}{W} \equiv \frac{1}{W} \cdot \frac{\partial P}{\partial \rho} \Big|_{s,Z} = 1 + \frac{\partial[\ln(W)]}{\partial Y} \Big|_{s,Z} \\ &= 1 + \frac{\partial[\ln(T)]}{\partial Y} \Big|_{s,Z} + \frac{\partial[\ln(N \cdot \Phi)]}{\partial Y} \Big|_{s,Z} \approx 1 + \Gamma_G \end{aligned} \quad (10)$$

The Grüneisen gamma Γ_G in relation (9) is usually not reported in the numerical TDR output, though the related thermodynamic derivative called GAMMAs (Γ_S) is reported. Utilizing the rule (10) requires that the Φ and A deviations remain negligible, as noted previously, yielding the wanted relationship, $\Gamma_G \approx \Gamma_S - 1$, in transposed form.

14 References

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