

Removing Booster Influences from Toxic Fumes

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ABSTRACT

This report investigates whether it is tractable and thereupon reasonable to remove the booster influences when ranking the toxic fumes of non-cap-sensitive mining explosives. The hazard potential is represented by relative fume toxicity RFT, the resultant influence computed from a formulated rule with a restricted set (tally) of fume components and multiplying constants. The RFT result is compared to the rule criterion that represents the worst case tolerable toxicity stipulated by regulations or otherwise. The typical nonstoichiometric booster composition can render notable unwanted influence on the RFT ranking results. Historically, the remedy was to shoot the booster separately and reduce the trial concentrations by the relevant subtractions. Unreal negative concentration results were noted on rare occasions, revealing the faulty nature of the reduction procedure. With thermodynamic reaction chemistry codes TDRC, on the other hand, the booster ingredients can be retained in or removed from the reactant tabulation, yielding reduction factors taken as the concentration ratios for the two circumstances. The underlying presumption regarding reduction factors is that the ratios of component concentrations with and without the booster ingredients when resolved theoretically ought to equal those rendered experimentally, when tractable. Upon rearranging the presumed relationship, the unadjusted fume concentrations divided by theoretical reduction factors yield the wanted readjusted fume concentrations, thereby removing the booster influence without generating unreal negative concentrations.

The work principle from thermodynamics restricted by the constraint of zero-net interaction loss is utilized in conjunction with the TDRC to resolve the wanted (Z-state) fume spectrum. This circumvents the recognized difficulty with traditional hydrodynamic detonation theory that is related to the nonideal reaction characteristics of typical mining explosives. The tacit characteristic of the Z-state resolved from the non-trajectory work principle is that it can not be remedied or tampered with, unlike the traditional trajectory techniques where the reaction products can be readjusted by changing formula representations, nullifying specific reactions or otherwise manipulating the thermodynamic trajectory process. Though the work principle theory is an unfinished formulation, the Z-state results prove worthy enough for rendering trends and comparisons and reaching otherwise useful conclusions. Further refinements should yield more reliable fume spectra and indicate explosive composition readjustments that would reduce toxic effects within underground mines and the wider world environment.

THE INTRODUCTION

Toxic fumes cause fatal and nonfatal incidents in underground mining, where the working environment tends to trap the fumes, restricting natural dilution or forced ventilation, thereby hindering the restoration of nonharmful work conditions. Though the undiluted fumes are relatively concentrated, their dangerous concentrations are reduced in time by dilution, cool reactions, or rock and dust absorption. Warnings related to the hazards of toxic fumes are found in reference books of the industry^{1,2,3}. Nonhazardous conditions have not always prevailed when work was resumed, resulting in serious or fatal incidents in underground operations⁴. Nominal workday threshold toxicity restrictions and other relevant information were utilized in a rudimentary ventilation model to yield typical waiting

times, roughly a few hours, required to restore nonharmful working conditions ^{5,6}. Though fume dissipation is relatively unrestricted for surface shots, the tremendous quantity and harmful nature of the reaction products can still have an unacceptable impact on the work force, nearby community, or the overall environment.

The relevance of the traditional hydrodynamic theory of detonation remains questionable for nonideal detonation of mining explosives, without some type of theoretical readjustment ⁷. The work principle of thermodynamics was reformulated with a constraint theory for resolving the remnant (close to last) equilibrium state of the reacting medium ⁸. The fume spectrum for mining explosives undergoing nonideal detonation and subsequent rapid combustion is then resolved with the TDRC. Theoretical results from the nontrajectory work principle and TDRC show respectable fit with a number of reported mine shots ⁸, so that outright refutation of the restrained work principle technique would be rather difficult. Theoretical trends for recent underground chamber shots noted later also yield rather comparable results. Notable differences that were observed were not wholly illogical and they could diminish with further refinements in the unfinished work principle theory.

The relative fume toxicity RFT rules utilized to yield hazard potentials and understand risks do not remove or replace the requirements or conditions set forth by relevant guidelines or regulations. Though the recent and older permissibility RFT rules are utilized in this report, forewarning is given that this has no bearing on regulation fume tests that are undertaken for cap-sensitive explosives which require no booster. It is worth noting that the RFT tally choices and formula multipliers are not unique and none of the rules incorporate the whole range of possible toxic components, yielding a wide range of hazard potential results that tends to cloud the risk issues. Regulation ranking tests tend to restrict the types of toxic problems, which ought not to be interpreted as rendering complete or useful measure of the hazards involved. Workers, therefore, need to remain cautious of hazardous circumstances, not just rule implications, for there are numerous and unexpected influences that govern the formation of dangerous toxic fumes ^{9,10}. The possibility of utilizing remote or portable instrumentation to monitor or detect multi-component toxic fumes should not be overlooked.

TRADITIONAL AND RECENT UNDERGROUND RFT RULES

The hazard potentials taken as results from formulated RFT rules utilize uniform notation and units, rather than their original guideline or regulation formats. The respective columns of Table 1 show the RFT reference or role name, the tag, formula and criterion. The RFT rules work with a restricted set (tally) of concentrations, the bracket terms within the formulas that represent fume component volumes per unit explosive mass. Reported test results are transformed to standard reference conditions of 25 °C and one atmosphere. For regulation testing, candidate explosives fail when RFT results exceed their criterion, which represents worst case toxicity tolerable, thereby denying their usage under the relevant mining conditions. The last column represents criterion with unit conversions from the original format to those for the Russian criterion (metric). The fume class requirements were transformed by stipulating the cartridge mass as 200 grams ¹¹. The graphical trends worked out later yield results that were normalized with respect to their criterion for convenience, so that reported test data or theoretical trend states under (over) unity would be regarded as tolerable (unacceptable).

The RFT-P rule multiplying constants are those required to render the carbon monoxide, CO, concentration for equivalent toxicity ¹². The Russian formula RFT-R is the widely recognized forerunner of the weighted rule formulations, with a nonunity multiplier taken in recognition that harmful influences depend upon the fume composition ¹³. The Russian rule is more tractable to

implement, though it would not yield a rigorous CO equivalent toxicity, unless the constant were replaced with a function of the NOX components. The unweighted resultant sum rules RFT-C without NOX and the RFT-U are retained, while the Fume Class II and III rules and the RFT-C' with NOX were not pursued further. Recently the TLV-TWA for CO was reduced from 50 to 25 ppm¹⁴, which without renormalization would double the CO multiplier. Renormalization would return the CO multiplier to unity, halve the remaining multipliers, and justify the same reduction in the rule criterion. These readjustments are not incorporated into the current regulations or guidelines and therefore were not utilized in our investigation.

| Table I. Traditional and Recent Underground RFT Rules & Criteria | | | |
|--|------------------|--|-----------------------|
| Reference Name | Relevant RFT Tag | Formula With Tally of Concentrations [cc/g] | Transformed Criterion |
| Recent US | RFT-P | $RFT-P = [CO_2]/100 + [CO] + 2 \cdot [NO] + 17 \cdot [NO_2] + 2 \cdot [NH_3] + 5 \cdot [H_2S] + 25 \cdot [SO_2]$ | 156 cc/g |
| Russian | RFT-R | $RFT-R = [CO] + 6.5 \cdot [NOX]$ | 50 cc/g |
| Old US | RFT-U | $RFT-U = [CO] + [NOX]$ | 156 cc/g |
| Fume Class I | RFT-C or C' | $RFT-C = [CO] + [H_2S]$ | 23 cc/g |
| Fume Class II | RFT-C or C' | Or | 47 cc/g |
| Fume Class III | RFT-C or C' | $RFT-C' = RFT-C + [NOX]$ | 95 cc/g |

ROLE OF MINING CONDITIONS AND UNDERGROUND TEST FACILITY

Numerous circumstances control the nature of toxic fumes: the type or grade of charge formulation, hole contaminates, mixture uniformity, water resistance, marginal initiation, stratum confinement, rock hardness, dust interactions, and other usage conditions^{1,2,13}. The surrounding stratum regulates the work output, reduces the rate of fume expansion, and temporarily traps the reaction products so that otherwise tardy reactions transpire. Hole-to-hole waves can marginally desensitize the charge formulation, resulting in unusual reaction kinetics and weak detonations^{15,16}. Under rift compression (or heave), some reaction gases are forcefully driven into the cracks and pores of the roof, walls and floor. Fumes trapped within the rock and dust can be released back into the working environment¹⁷. Recognition was taken that the carbon oxides tend to increase with hard rock confinements, while the nitrogen oxides tend to increase in cracked or friable rock conditions¹⁸.

Traditional techniques for measuring toxic fumes from cap-sensitive explosives would not work for blasting agents, which normally require larger charge diameters and total masses to shoot properly and yield typical fumes. Recently an underground test chamber was developed for measuring toxic fumes from those blasting agents¹⁹. The underground NIOSH fumes facility has a 274-m³ chamber, which contains 324-kg air within the walls. The mining explosive under test has a typical mass of 4.54 kg confined by a 10.2-cm diameter cylindrical steel pipe for proper detonation. Though the typical 172-g pentolite booster is roughly 4% of the trial explosive weight, it can have a notable influence on the fume spectrum. Traditionally the booster influences were removed by shooting it separately and subtracting off the corresponding fume components²⁰. The resulting nonphysical negative concentrations noted on rare occasions warn of the faulty nature of this remedial technique.

TROUBLES WITH TRADITIONAL THEORY AND NONEQUILIBRIUM

The nonideal detonation of mining explosives^{21,22} is not reconcilable with the traditional requirements of the Zeldovich von Neumann Doering (ZND) theory. For the unmodified ZND theory, the reaction thermicity reduces to zero upon reaching the Chapman Jouguet CJ sonic condition. Nonideal explosives react through the transonic region, so the zero-thermicity requirement is a recognized conflict, resulting in a numerical infinity. Incorporating some representative loss term in the ZND formulation can render the difficulty moot, so the relevant theoretical relationships remain numerically bounded⁷. The resolution raises questions regarding the true reaction process undertaken and renders some philosophical room for invoking the work principle from thermodynamics^{23,24}. For rock mining or chamber testing, the restoring influences that try to uphold mechanical and thermal equilibrium rapidly widen the zone of fumes within the surrounding medium, via Le Châtelier's principle²⁵. Under the transitory circumstances with declining zone temperatures the relaxation times for chemical reactions rise drastically and the restorative forces trying to sustain chemical equilibrium falter. Wall or dust interactions, or other types of residual nonequilibrium reactions persist noticeably at the cooler temperatures in the underground chamber within the hour of measurement, ruining the presumption of terminated reactions. Trying to reckon the last respectable remnant or state of total thermodynamic equilibrium for TDRC resolution now turns into a worthwhile undertaking.

Thermodynamic reaction chemistry codes TDRC yield results only for total equilibrium circumstances and they would therefore not be appropriate for resolving the nonequilibrium circumstances. Reaction restrictions like frozen-flow are usually imposed for chosen temperatures on the late stage (post-CJ) trajectory to inflict a reaction type of constrained equilibrium. Reckoning the fumes by tracking the thermodynamic trajectory downward from the high-density region could be wrong or unreliable, if the equation-of-state EOS formula is ill founded, yielding undesirable results for ranking their toxicity. The work principle can not be tampered with or remedied in this fashion.

WORK PRINCIPLE FOR PREDICTING TOXIC FUMES

The work principle, which is described more thoroughly in the Appendix, was developed for theoretically resolving toxic fumes from the nonideal detonation of charge formulations. The whole description of wanted process refers to macroscopic changes resulting from removing and imposing thermodynamic constraints that work chronologically to render trajectory key states. The work principle utilizes a quasi-potential or negative work function, with numeric resolution requiring a TDRC for the terminal thermodynamic regime under consideration. The work principle method is unable to restrict reactions, tailor the work output or otherwise resolve states within the jump transitions, so that the trajectory terminology is utilized only in a figurative way. The work principle incorporates a working fluid that interacts irreversibly with a tremendous reservoir or reversibly upon a mechanical agent^{23,24}. For modeling underground fume tests rather than rock blasting or other circumstances, the working fluid represents the reaction ingredients undergoing transformation to resulting products within the fume zone. The reservoir represents the underground chamber walls and the contained air. The mechanical agent remains an uncorrelated item in our restricted interpretation⁸.

Rather than coping with the hard issues of nonequilibrium, the toxic fumes were resolved numerically for the Z-point, rendered by a zero-net-interaction constraint. Though ZND techniques require complex equation-of-state EOS for the whole trajectory from the original dense reactant state, the work principle formulation requires an EOS that works just for resolving the terminal key state. The resulting rarefied, thermally hot Z-state is reconcilable with the ideal gas domain, therefore the TDRC that was used for

resolving the fume spectrum was the NASA Lewis Complex Chemical Equilibrium Code. This TDRC works with idealized forms of condensed phases and gas mixtures; it has a wide range of molecular species²⁶ and on occasion reveals unexpected toxic components not recognized by the RFT rules or detection equipment. Resetting the EOS formula or constants would be rendered ineffectual with the form reductions taken for the ideal regime, which makes it hard to remedy or to tamper with the work principle. Furthermore readjustments within the trajectory transition such as restricting certain reactions are forsaken, and the trajectory key state is rendered as a result, not an optional choice. The reduction factors, the ratios of Z-state concentrations, were taken from the non-trajectory work principle method rather than the more traditional trajectory techniques, thereby nullifying uncertainty or dispersion due to finagling manipulations.

RELEVANCE OF FUME COMPONENT STABILITY

The unfinished work principle model is unable to resolve the unstable fume components, so it is fortuitous that the hazard potentials taken as RFT rule results are not normally dominated by those components. The original Z-state concentrations remain relatively unchanged for more stable components during transition to the Q*-state, representing measurement conditions in the underground chamber. The reaction products with noteworthy concentrations that were diagnostically useful were carbon dioxide CO₂, carbon monoxide CO, hydrogen H₂, and the total nitrogen oxides, NOX. Though nontoxic, H₂ represents a notable fraction of the reliable and useful test information and therefore was retained. Relatively weak concentrations of ammonia, NH₃, and methane CH₄ were observed; they remain negligible for the theoretical results and of little bearing on the RFT conclusions reached. Within the measurement hour, nitric oxide NO transforms rather quickly to nitrogen dioxide, NO₂, so they were regarded as unstable. The resultant sum NOX tends to remain more constant, though recent underground tests with dynamic instrumentation have revealed trends for its rate of disappearance, making its constancy suspect and warning of some difficulty with our resolution method.

REACTANT AIR AND 'R' THE CHEMICAL EQUIVALENCE RATIO

Theoretical TDRC trials to remove the booster influence were resolved without and with the inclusion of reactant air, wherein the oxidation noticeably reduces r the chemical equivalence ratio. This ratio depends upon the negative and positive oxidation states of the chemical elements in their commonly occurring compounds^{27, 28}, where only one or none of the oxidation states is nonzero. When r is over unity without air ingestion, r is reduced to unity by raising the quantity of reactant air, which is referred to as with (or 100%) reactant air or r -stoichiometry. When r is under or equal to unity without air ingestion, the ingestion is forsaken and r remains unchanged, which is referred to as zero (no or 0%) reactant air. The ratio of reactant air mass to total reactant mass, with the booster if utilized, is designated RAX. Typical RAX numbers for r -stoichiometry were 0%, 25% and 50% for roughly 5%, 8% and 10% fuel oil respectively. The original zone dimensions for the reactant air reside within those for the resulting Z-state fume zone, so that the requisite ingestion occurs without unnatural mass transfer. The terminology reactant air is retained as a reminder that it now represents a working fluid component that otherwise was a tiny portion of the underground reservoir that represents the tremendous non-reactive (inert) component in the work principle model.

SUPERPOSITION RULE FOR INCOMPLETE AIR INGESTION

The zone of fumes is regarded as rapidly formed, so that the reactant air for r -stoichiometry noted within the TDRC ingredient table might not be wholly consumed upon reaching the Z-state. Originally,

theoretical trends from the work principle in conjunction with the reported test data raised concerns about reactant air significantly modifying the fumes. Though the work-principle could not resolve the incomplete reaction states in an obvious way, numerical superposition of the two resolvable cases with 0% and 100% reactant air could yield the wanted intermediate circumstance. The multiplying constants in the superposition formula were resolved by regarding the fume zone as spherically symmetric. Within the fume zone the reactant air consumption was taken as proportional to fractional distance to the zone surface, ranging from 0% at the zone center to 100% r-stoichiometry on the zone surface. Averaging the radial fraction over the spherical zone yields the number 75%. The resultant fumes therefore were taken as though 75% utilized 100% reactant air and the residual 25% utilized 0% reactant air. The wanted intermediate concentration $X(k)$ of the k th fume component is then determined by the two tractable work principle concentrations $X(k)$ using the following relation.

$$X(k)_{\text{Reactant Air 75\%}} = 0.25 \cdot X(k)_{\text{Reactant Air 0\%}} + 0.75 \cdot X(k)_{\text{Reactant Air 100\%}}$$

Rate consumption proportional to the N th power of the radial fraction would also be worth investigating though it would be illogical to expect that graphical trends from the unfinished work principle could optimize the choice of N , while other recognized and notable shortfalls remain unaccounted for.

RESULTS WITH THE BOOSTER INGREDIENTS

Without the superposition rule, four types of theoretical results were originally resolved for comparison with the reported test data: (1) no reactant air and no booster, (2) with reactant air and no booster, (3) no reactant air with the booster, and (4) with reactant air and with the booster. The quest was to determine which choice most closely represented the phenomena observed in the underground fume chamber. For convenience, the graphical plots are subdivided into three regimes: the lean range (under 4%), the mid range (4–7%), and the rich range (over 7%), where numbers within parenthesis refer to the fuel oil [%] in the ammonium nitrate fuel oil ANFO. Retention or removal of the booster influence was ultimately understood from trend comparisons in the lean range, where the r-stoichiometry was under unity and reactant air was unnecessary and therefore not relevant. The role of reactant air ingestion was ultimately understood by trend comparisons in the rich range, where retention or removal of the booster ingredients hardly modified the overwhelming contributions from the rich trial explosive.

The graphs in Figures 1 through 4 show the test results and theoretical trends for CO_2 , CO , H_2 , and NOX concentrations [$X(\text{cc/g})$] with respect to fuel oil [%], with the booster ingredients retained. The 75% superposition rule was utilized to forecast the intermediate graphical trend, which was naturally straddled by those for zero reactant air and r-stoichiometry. The theoretical trends remain identical without reactant air in the lean range with r under unity, until the r reached unity in the mid-range when the branching occurred. For higher fuel percent, the r-stoichiometry was restored to unity for the 100% reactant air trend. Notice that the 75% reactant air trends for CO_2 , CO , H_2 , NOX were over, under, under, and over the undrawn trend through the reported test data (dark circles). Under (over) refers to the graph's ordinate direction taken to reach zero (100%) reactant air. With half the residual differences in opposing directions, there was no readjustment that would tremendously reduce the net deviations or notably improve the formulated superposition rule.

The reported test results for the four more stable components were closest to the 75% trend, except H_2 which was closer to the 100% trend, so it was rather obvious that ingested air played a notable role in

the overall reaction process. The H₂ data could have strayed as the result of unmixing or disappearance from the underground chamber. With the reported test information related to the theoretical trends, the reaction with air was revealed, implying that the mining explosives had undergone nonideal detonation. Upon reaching the transonic CJ region the reaction mechanics were incomplete, so notable combustion transpired thereafter, utilizing trapped air in the rapidly widening fume zone. Roughly 75% reactant air was consumed reaching the last remnant of equilibrium Z-state, whereupon the more stable components remained roughly unchanged.

RESULTS WITHOUT THE BOOSTER INGREDIENTS

The graphs in Figures 5 through 8 show the test results and theoretical trends for CO₂, CO, H₂, and NOX concentrations [X(cc/g)] with respect to fuel oil [%], without the booster ingredients. The reported charge formulation results (dark stars) without the booster were resolved using the reduction factor technique, discussed shortly. The rationalization noted previously still explains why the trends start-out identical, branch-out and then undergo wider divergence. The 75% reactant air trends for CO₂, CO, H₂, NOX over, under, under, and over the undrawn trend through the reported results, so readjusting the superposition constants still would yield no benefit. The residual differences between the reported test data and their corresponding theoretical traces remained roughly unchanged regardless of whether the booster ingredients were retained or not.

For the graph in Figure 9, the resultant sum of concentrations of CO₂, CO, and CH₄ were taken, representing the reaction products that retained the majority of carbon {C*}. Theoretical CH₄ concentrations were negligible and rendered no worthwhile influence on the resultant sum, while the reported CH₄ results had only a little influence on the resultant test information. The traces without (with) the booster were remarkable fits to the readjusted (unadjusted) data over the whole range of fuel percent, regardless of the reactant air taken. The readjusted trend without the booster tended to zero intercept for zero percent fuel oil, which is logical if that is the only remaining compound containing carbon. Technically carbon type fumes could have occurred from the reaction of wrapping tape or wire insulation, but the roughly zero intercept with the transformed readjusted information suggests those effects were rather minor.

THE REDUCTION FACTORS

Traditionally the booster influence was removed by subtracting the booster fume components from the corresponding unadjusted test results, which would yield readjustments of a few percent here. Undoing the superposition of the mixture with subtraction is questionable when there are notable compositional differences and the Z-state temperature for just the booster reaction is roughly a thousand degrees hotter than for the charge formulation, implying different reaction kinetics. Quite to the contrary, the compositional weight percentages and Z-state zone temperatures for the charge formulation with and without the booster ingredients remain roughly similar, as would most of the reaction kinetics. Regardless of the reactant air r-stoichiometry condition taken, the following relation defines the reduction factor for the kth fume component.

$$\text{Reduction Factor}(k)|_r = \left[\frac{X(k)_{\text{With Booster}}}{X(k)_{\text{No Booster}}} \right]_{\text{Reactant Air } r \text{ Condition}}$$

The theoretical concentrations $X(k)$ were normalized by the formulation charge mass under test, without the booster mass, regardless of whether it was in the TDRC ingredient tabulation. The underlying presumption regarding reduction factors is that the ratios of component concentrations with and without the booster ingredients when resolved theoretically ought to equal those rendered experimentally, when tractable. Transformations of results to the standard reference conditions are implied. Therefore by rearrangement, the unadjusted fume concentrations divided by resolved theoretical reduction factors would yield the wanted readjusted fume concentrations. The reduction factors formed theoretically could never be negative and therefore unlike the traditional subtraction method could never reverse the numerical sign when transforming the reported test concentrations (normally positive). The unadjusted test concentrations could be negative if they were rendered by subtraction of imperfect instrumentation results, like $[NO] = [NOX] - [NO_2]$.

The reduction factors required the theoretical concentrations from the graphs referred to previously, so their discussion was postponed until now. Reduction factors can have unexpected nature because of the nonlinearity of the relations characterizing the complex chemical reactions, so different circumstances of air ingestion were investigated as noted in Figures 10, 11 and 12. Though the reduction factors stayed under 14, the ordinate scale was restricted to 7 so overlap regions would have more graphical resolution. Reduction factors for the k th component remained identical within the lean range, where reactant air was not required. For the rich range, the reduction factors tended to unity, though NO, NO₂ and their sum NOX were notable exceptions, revealing untypical divergence. The graphical trend dispersion for 75% reactant air resembled the r-stoichiometry case rather than the zero reactant air case. Reduction factors were normally over unity so the readjusted results were normally diminished, though the reverse case of augmented results is not ruled out for the nonlinear relationships that characterize reaction processes.

FORECASTING THE RELATIVE FUME TOXICITY

With the work principle, the thermodynamic mixture state can be rendered for a chosen circumstance. The reduction factors with 75% reactant air were taken to resolve the hazard potentials, since the related concentrations resembled the reported test data more closely overall. The RFT results shown in Figures 13 through 16 were computed from their formulas in Table 1 for the relevant tally of unadjusted or readjusted concentrations. They were then normalized with respect to the rule criterion. The readjusted test data (dark stars) ought to be compared to the theoretical trends without the booster (dashed traces), while the unadjusted test data (dark circles) ought to be compared to the theoretical trends with the booster (solid traces). Often the reduction factor corrections were minor, so the dark circles hid the dark stars. The reported test data or trend points on the normalized graphs that were under (over) unity represent tolerable (unacceptable) circumstances, so that the charge formulations had okay or not-okay hazard potentials, depending upon the RFT rule invoked.

The RFT-C graph in Figure 13 and Figure 5 resemble each other because the Fume Class rule without H₂S would just yield renormalized CO information. The RFT-C results under unity in the lean regime would pass the fume class requirement, while those over unity in the rich regime would not. For the RFT-U trend, Figure 14, the reported and theoretical information universally remain under unity and therefore pass the older US toxicity test. The restricted form of the unweighted RFT rules are unable to reflect the differential toxicity within their tally of components, and they tend underestimate CO equivalent toxicity when compared to rules with nonunity multiplying constants⁵. The theoretical trend results for the Russian rule in Figure 15 show relatively close fits with the reported test data. With the

trends near unity, it would be imprudent to suggest that the unfinished work principle method has sufficient resolution to render with certainty such crucial ranking decisions.

The recent permissibility rule RFT-P results in Figure 16 remains an isolated phenomenon that reveals the dismal tragedy of utilizing an unfinished theory for determining relative fume toxicity when the formula rule depends upon relatively unstable components. It is worth recalling that the reduction factors were resolved for the thermodynamic Z-state, and that would yield wrongful information for the unstable components that transform noticeably during their transition towards the nonequilibrium Q*-state. The ill-conceived reduction factors for NO and NO₂ utilized in conjunction with their nontrivial measured concentrations rendered the graphic misfit. Recognition need be taken that the Z-state from the work principle remains rather inflexible and not open to remediation, while a trajectory type theory could be tampered with to yield closer fits for reported test data in the last graph.

CONCLUSIONS AND RECOMMENDATIONS

The technique for removal of booster influences rests upon the presumption that the reduction factor or concentration ratio with and without booster ingredients would be identical whether they were resolved theoretically or experimentally. The reduction factor was tractable theoretically, just by removing booster ingredients from the TDRC tabulation, though it could not be resolved experimentally for the chosen charge formulations. The relationship could be confirmed with cap-sensitive charge formulations that were shot with and without the unnecessary booster. From the graphical inspections it was recognized that the residual differences of the theoretical trends without or with booster ingredients respectively were comparable for the readjusted or unadjusted test data. Whence, the reduction factor technique is tractable, without revealing any strong tendency to worsen or improve the residual differences between theoretical and reported information. There were no noteworthy revelations inferred from the removal technique that were not rendered without it, except for the reckoning of the zero intercept on the readjusted {C*} trend. Working with the unadjusted observations and trends minimizes the computational hardship and number of presumed conditions. Therefore the retention of the reduction factor technique is not recommended unless the regulations or guidelines stipulate toxic fume results with the booster influences removed.

The work principle technique with the zero-net interaction restriction yielded trends with reactant air that were comparable to the reported fume results in the underground test chamber. Originally this raised concerns that the fumes results were modified by reactions from air ingestion. Further research with restricted oxygen shots was started to understand this influence. The rationale for incomplete reactant air ingestion was that the fume zone undergoes rapid expansion until reaching the last remnant of equilibrium state, without fully utilizing the quantity of reactant air reckoned from r-stoichiometry. It is worth noting that the original zone dimensions for the reactant air reside within those for the resulting Z-state fume zone, so that the requisite ingestion occurs without unnatural mass transfer. Numerical coefficients for the superposition rule were resolved utilizing a proportional relationship, yielding the Z-state mixture rule with r-stoichiometry results weighted at 75% and the residual no reactant air results weighted at 25%. The trends and reported test results supported the notion that reactant air was involved in a notable way with the combustion transpiring after the transonic CJ state, indirectly confirming that the detonation reaction was quite nonideal.

The tentatively unfinished work principle yields results for the RFT-C, RFT-U or RFT-R formula, which were not unreasonable. The trends for the 75% r-stoichiometry were utilized, regardless of whether the retention or removal of the booster influence information was taken. Reported fume

concentrations and theoretical trend information for a charge formulation with a chosen fuel percent reveal the non-unique okay or not-okay nature of the different hazard potentials. The reduction factor technique was workable though there were notorious ill-fitting revelations when the RFT-P formula was investigated. The requisite unstable fume components NO and NO₂ within the RFT-P rule were recognized to cause the worst difficulty.

The unrefined work principle remains useful for resolving the Z-state taken as the last remnant of total equilibrium, though the nonequilibrium Q*-state remains intractable. Recommendations that the unfinished model incorporate a non-zero reservoir interaction (N-state), and the transitional rate kinetics for N—Q* (or rougher Z—Q*) jump to reach the non-equilibrium Q*-state should be pursued. Thereupon, the optimization Nth order rate rule for the r-stoichiometry-mixing rule would be worthwhile, if the refinements reduce the residual differences and resolve the unstable nonequilibrium states.

APPENDIX: THERMODYNAMIC THEORY UNDERLYING WORK PRINCIPLE

The work principle incorporates a working fluid that interacts irreversibly with a tremendous reservoir or reversibly upon a mechanical agent. The working fluid can have a reactive composition, transfer heat to or work upon the reservoir or work upon the mechanical agent in a reversible nonexpansion way, though the reservoir is unable to interact directly with the mechanical agent. The reservoir must retain constant thermal mechanical characteristics and therefore have tremendous (mass) proportions compared to the other two components. None of the components interchange particles so the working fluid mass remains constant, which is useful for renormalizing other thermodynamic quantities. The resolution utilizes constraints that work chronologically, though they are not required to formulate the unrestrained work principle. The work principle incorporates a quasi-potential, Y_Q, or negative work function [-W_F], written per unit working fluid mass, since TDRC render their numeric results that way. The work function and quasi-potential terminology tend to be redundant though useful forms, defined by the relation:

$$-W_F \equiv Y_Q \equiv \left[U - T_R \cdot S + \frac{P_R}{\rho} \right]$$

The quasi-potential Y_Q (or W_F) depends upon the working fluid's energy per unit mass U, entropy per unit mass S and density ρ (Rho). Neither the quasi-potential nor the work function qualifies as a state function of the working fluid since they depend upon reservoir characteristics, temperature T_R and pressure P_R, despite their requisite constancy²⁹. The resulting construction of the quasi-potential, represented as a superposition of working fluid state functions with constant reservoir multipliers, is independent of the trajectory pathway, regardless of process irreversibility or nonequilibrium, and therefore has formidable theoretical capacity. The work principle inequality relation taken from the noted references²⁴, is then

$$\text{Work} \leq \Delta W_F \equiv \Delta[-Y_Q]$$

The work done by the working fluid upon the mechanical agent, **Work**, would equal the work function rise ΔW_F or Δ[-Y_Q] for a reversible path, and the inequality would hold for irreversible process. Restoration work refers to the work that would be rendered by (not upon) the mechanical agent to reversibly return the working fluid to its original thermodynamic state. Noting the restoration work is a

way to recognize the working fluid's propensity for undergoing transformation via chemical reaction³⁰. The resulting work done upon the mechanical agent over a whole cycle would be zero or negative, **Work** ≤ 0, regardless of the process undertaken. Therefore, the mechanical agent would render the restoration work forever, without taking recourse in the reverse possibility, forbidding any prospect of a perpetual motion machine.

Natural processes are regarded as macroscopic (non-infinitesimal) transitions that are somewhat irreversible, however slight, with or without reversible fluctuations. For resolving toxic fumes, restriction is taken to natural processes with no **Work**, as though the mechanical agent was dysfunctional. Technically the mechanical agent is not removed from the work principle model, just rendered moot, so it is unnecessary to identify some contraption in the reaction process or underground fumes chamber with it. Under this restriction, the work principle relation reduces to

$$\Delta W_F \geq 0 \quad \text{or} \quad \Delta Y_Q \leq 0$$

For a natural process without the mechanical agent to render restoration work, it is impossible to return to the starting state. Restoration work remains an illusion that requires the reverse process, with the opposite and wrong chronology. With normal chronology, the reduction in the quasi-potential $\Delta[-Y_Q]$ or the rise in the work function ΔW_F registers the restoration work that would be necessary to undo the deterioration.

RENDERING OF IMPOSED CONSTRAINTS

The rendering of imposed constraints refers to the utilization of relative minimum trapping conditions to stall the trajectory motion. The Y_Q partial derivatives taken with respect to the unrestrained χ , while holding κ constant, form the constraint representation with thermodynamic state variables. The unrestrained infinitesimal change $\delta\chi$ taken while holding κ constant would remain unrestricted were it not for the requisite reduction of the quasi-potential. The change of the quasi-potential Y_Q or negative work function W_F is resolved according to a Taylor's expansion in unrestrained χ , while κ remains constant with normal (not reverse) chronology understood³¹.

$$\delta[-W_F]_{|\kappa} \equiv \delta Y_Q|_{\kappa} \equiv \sum \frac{(\delta\chi)^J}{J!} \cdot \frac{\partial^J Y_Q}{\partial \chi^J} \Big|_{\kappa} \leq 0$$

Technically, the subscripts should bear witness to the restriction of chemical equilibrium, though that requirement is universal for our terminal 'key' state resolution, so the reduced notation just displays the κ constraint. Retention of only the lower order J terms is required for resolving and interpreting the transformations, as noted by the grave accent on the summation symbol. For resolving the minimum trapping state, $\partial Y_Q / \partial \chi |_{\kappa}$ would reduce to zero, while $\partial^2 Y_Q / \partial \chi^2 |_{\kappa}$ would be positive. The multiplication of nonzero unrestrained $\delta\chi \cdot \delta\chi$ with positive $\partial^2 Y_Q / \partial \chi^2 |_{\kappa}$ yields the wrong sign for the inequality relation. The only workable solution requires that the unrestrained $\delta\chi$ reduce to zero, which represents stalled trajectory motion, until the constraint is replaced with a different restriction or unrestrained travel occurs towards the reservoir state.

NON TRAJECTORY AND THERMODYNAMIC UNCERTAINTY

Irreversible and reversible fluctuations render the chronological occurrences that force the reduction of the quasi-potential, though there are other rationale for the retention of pathway uncertainty, including the quantum mechanics uncertainty principle and the relatively unknown thermodynamic statistical uncertainty principle³². Uncertainty principles render trajectory notions obsolete and force worst case minimum tolerances on canonically conjugate variables. Though our restrained and unrestrained variable functions do not necessarily form a canonically conjugate pair, there remains an underlying uncertainty in the working fluid state functions from which they were formed. Trajectory intractability remains the relevant issue not the obvious fact that TRDC results are fraught with much greater numerical errors than those imposed by the uncertainty restrictions.

ZERO-NET-INTERACTION ENERGY CONSTRAINT

For zero-net-interaction energy, the terminal trajectory state is resolved by requiring that the working fluid retain or recover the working fluid energy U_1 of the original and unreacted thermodynamic state. Within the trajectory transition, work done upon or heat transfer with the reservoir is unrestricted and could render nontrivial influence, while registering no net effect. With reservoir interaction, no restriction regulates the working fluid's entropy change, though transformations that would cause a rise rather than reduction in the quasi-potential are forbidden. The restriction on the terminal trajectory is written $U = \kappa$ for theoretical resolution, with $\kappa = U_1$ for the numerical resolution using the relevant TDRC. Utilizing hindsight, the forthcoming results were reduced in form with the K-function defined as $K \equiv P/R^*T$ where R^* is the Universal Gas Constant. Upon reaching the reservoir state, the K-function would equal the constant $K_R \equiv P_R/R^*T_R \equiv 40.874 \mu\text{mol/cc}$ (or mol/m^3). The reciprocal of K_R would equal 24,470 cc/mole for reservoir conditions taken at the standard reference conditions. For the unrestrained variation the entropy $\chi = S$ or the logarithmic density $\chi = y$ respectively yield,

$$\delta[-W_F]_{|U} \equiv \delta Y_{O|U} = (-T_R) \cdot \delta S \cdot \left[1 - \frac{K_R}{K}\right] = \left(\frac{T_R W}{T}\right) \cdot \delta y \cdot \left[1 - \frac{K_R}{K}\right] \leq 0$$

The working fluid and reservoir are regarded as thermal mechanical stable substances so their state functions like $W \equiv P/\rho$, T , or T_R are restricted to the positive range. Zero temperature is unattainable according to the third law of thermodynamics. The bracket terms arise regardless of the way the unrestrained χ was chosen, rendering a nonzero result for nonequilibrium circumstances and reducing to zero for constrained equilibrium. For explosion (implosion) type processes, the K-function is greater (less) than the reservoir constant, K_R , and the brackets are positive (negative), so the entropy S must rise (fall) and the density ρ must fall (rise), ultimately yielding $K = K_R$ for the trapping minimum. With the work principle, the restrictions imposed by the bracket terms from the trapping minimum requirement hold for any working fluid regardless of its equation of state EOS. The tenability of the restrictions remains unaffected when studied numerically, though results are worthwhile only if the chosen TDRC and related EOS characterize the working fluid in the thermodynamic domain under investigation. The working principle is resolved numerically by trial and error with TDRC retaining results, which reduce and ultimately minimize the quasi-potential.

When the zero net interaction Z-state constraint is removed, unresolved nonequilibrium circumstances prevail, though the restorative influences must ultimately recover the requisite $K = K_R$ circumstances at the reservoir conditions. Real gas formulations evaluated at the Z-state condition reduce to the unique

ideal form, which is wholly compatible with the rarified and thermally hot state. Under such circumstances, the work principle renders the Z-state molar density of the reaction fumes equal to K_R , regardless of the charge formulation, and forecasts that it would ultimately reach that result for the reservoir conditions. When the nonequilibrium working fluid transitions to the reservoir conditions, notable quantities of condensed phases (i.e. water) are normally incurred, thereby ruining the ideal gas presumption and the recovery of the molar density K_R at the reservoir Q^* -state.

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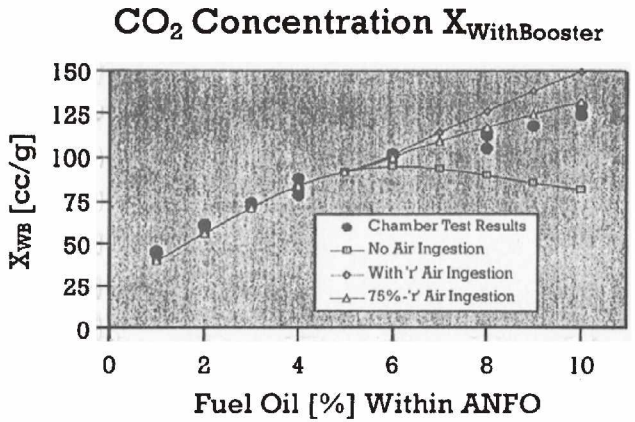


Figure 1. With-booster concentration X_{WB} [cc/g] of carbon dioxide CO₂ versus fuel oil [%] in ANFO.

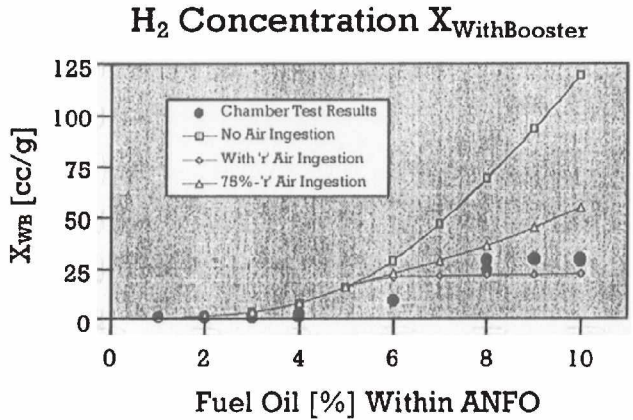


Figure 3. With-booster concentration X_{WB} [cc/g] of hydrogen H₂ versus fuel oil [%] in ANFO.

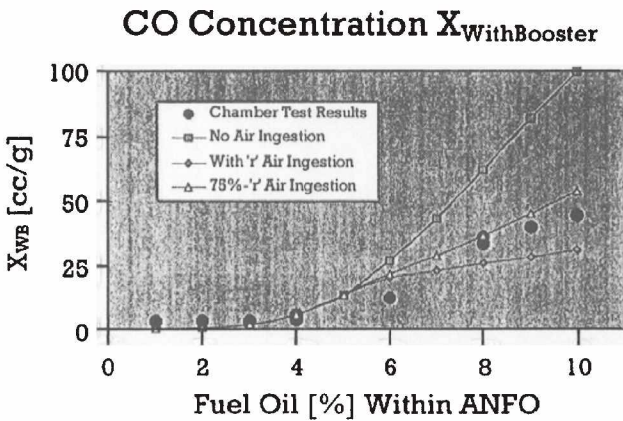


Figure 2. With-booster concentration X_{WB} [cc/g] of carbon monoxide CO versus fuel oil [%] in ANFO.

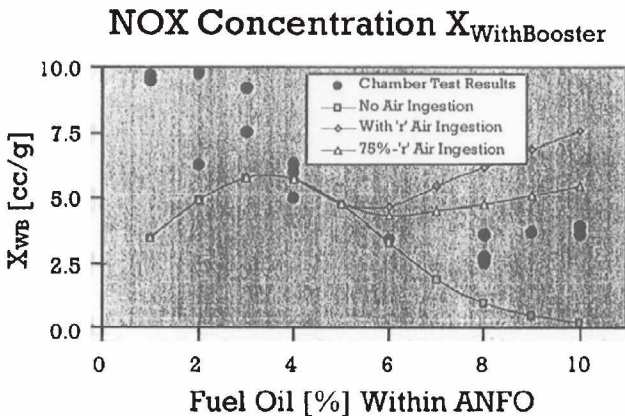


Figure 4. With-booster concentration X_{WB} [cc/g] of nitrogen oxides NOX versus fuel oil [%] in ANFO.

CO₂ Concentration $X_{\text{NoBooster}}$

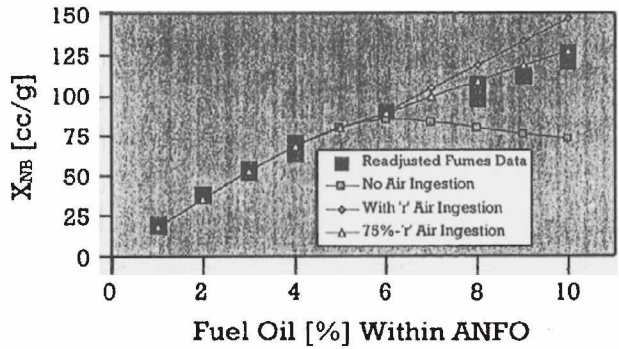


Figure 5. No-booster concentration X_{NB} [cc/g] of carbon dioxide CO₂ versus fuel oil [%] in ANFO.

H₂ Concentration $X_{\text{NoBooster}}$

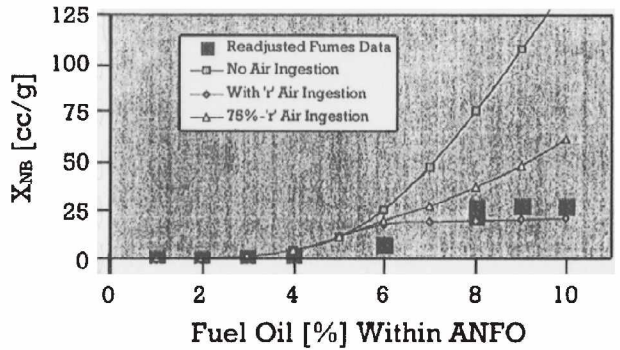


Figure 7. No-booster concentration X_{NB} [cc/g] of hydrogen H₂ versus fuel oil [%] in ANFO.

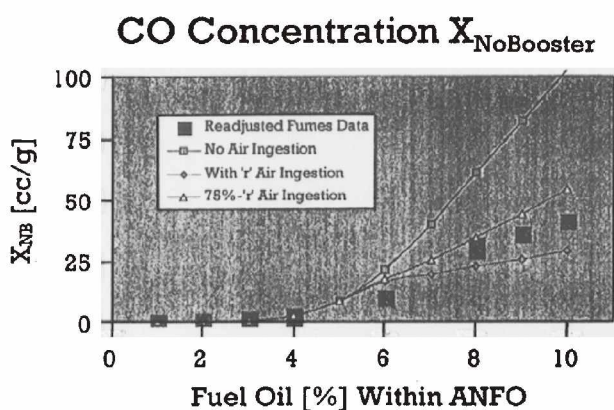


Figure 6. No-booster concentration X_{NB} [cc/g] of carbon monoxide CO versus fuel oil [%] in ANFO.

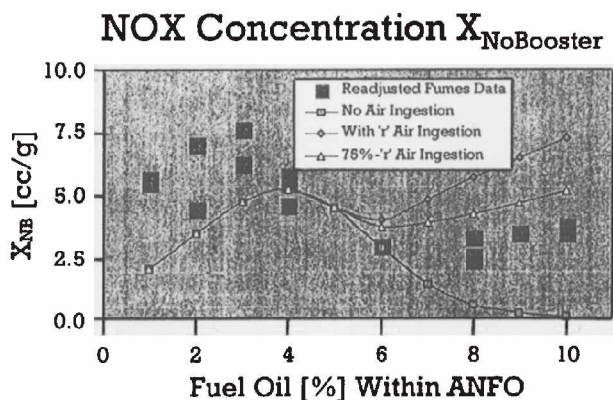


Figure 8. No-booster concentration X_{NB} [cc/g] of nitrogen oxides NOX versus fuel oil [%] in ANFO.

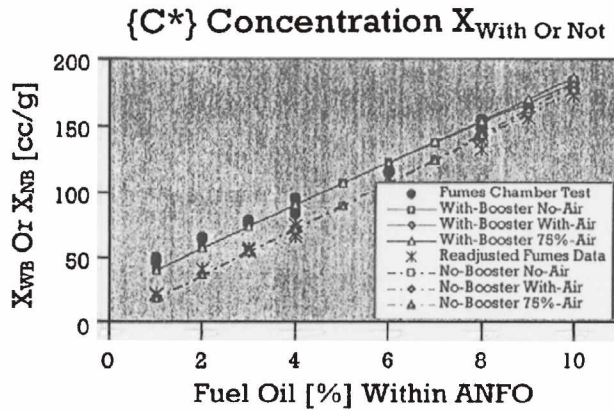


Figure 9. The concentration [cc/g] of the major carbon compounds versus fuel oil [%] in ANFO.

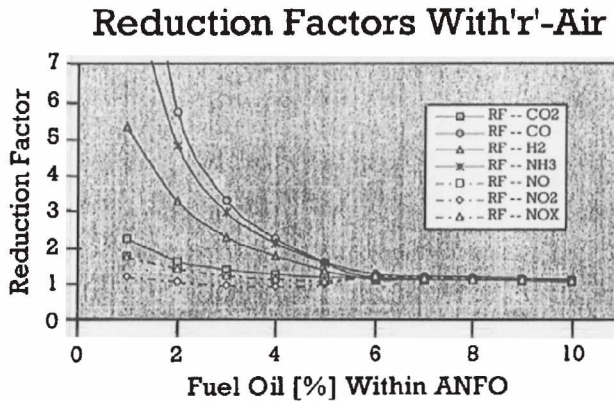


Figure 11. The reduction factors with 'r' reactant air ingestion versus fuel oil [%] in ANFO.

Reduction Factors No-Air

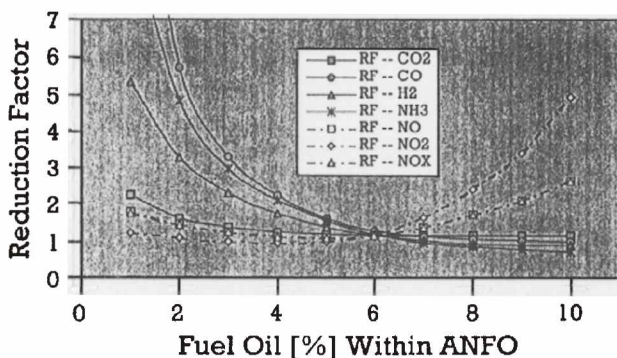


Figure 10. The reduction factors for no 'r' reactant air ingestion versus fuel oil [%] in ANFO.

Reduction Factors 75%'r'-Air

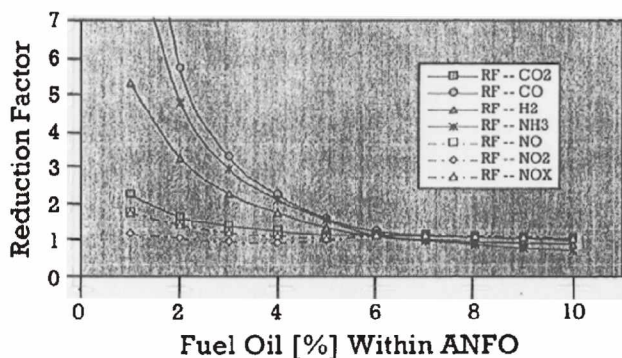


Figure 12. The reduction factors with 75%'r' reactant air ingestion versus fuel oil [%] in ANFO.

Normalized Relative Fume Toxicity The Fumes Class I Rule

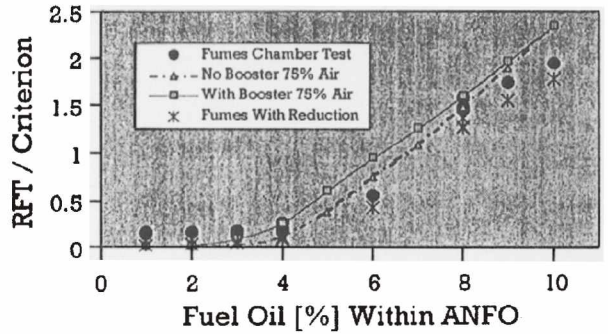


Figure 13. Fumes Class I RFT results normalized with the rule criterion versus fuel oil [%] in ANFO.

Normalized Relative Fume Toxicity Russian Underground Fumes Rule

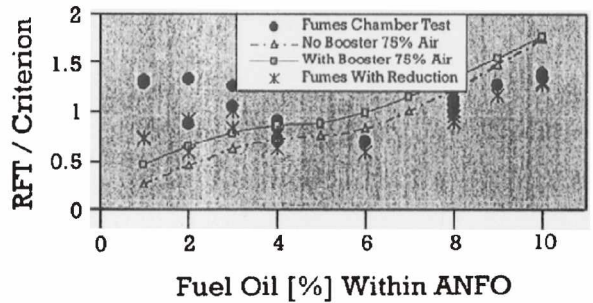


Figure 15. Russian Fumes RFT results normalized with the rule criterion versus fuel oil [%] in ANFO.

**Normalized Relative Fume Toxicity
Older US Permissibility Rule**

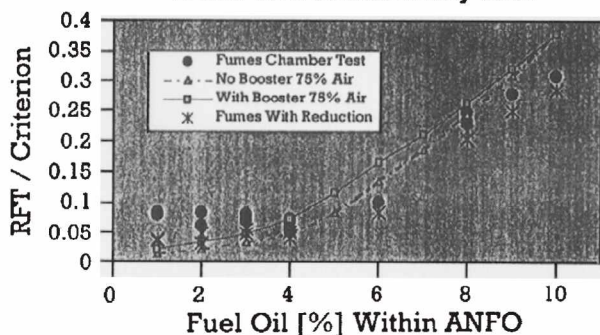


Figure 14. Older US permissible RFT results normalized with rule criterion versus fuel oil [%].

**Normalized Relative Fume Toxicity
Recent US Permissibility Rule**

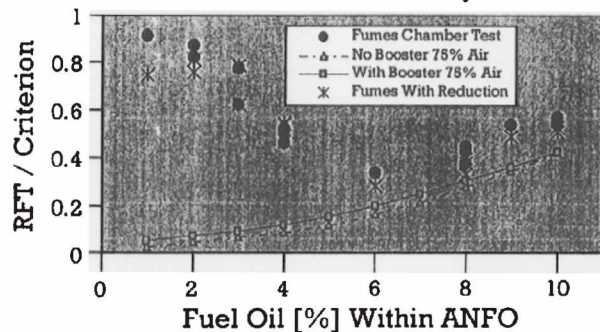


Figure 16. Recent US permissible RFT results normalized with rule criterion versus fuel oil [%].