Understanding the Hazard Potentials of Toxic Fumes

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ABSTRACT

Toxic fumes cause fatal and nonfatal incidents in underground mining, where the working environment tends to trap the fumes, hindering the restoration of nonharmful conditions. Workers can underestimate the residual fume toxicity and return to the work site too quickly. The toxic fumes from charge explosions depend upon a number things: formulation ingredients, mixture uniformity, water resistance, hole contaminates, rock hardness, and dust interactions. Hole-to-hole shock waves and rift compressions can partially desensitize charges, ruin the reaction kinetics, and worsen the fume toxicity. Traditionally the fume hazards for candidate explosives are resolved for a restricted set or tally of theoretical or measured fume components, transformed to standard reference conditions. The relative fume toxicity RFT is the resultant influence reckoned from a formulated sum of concentrations within the tally that are unweighted or weighted with chosen multiplying constants. The RFT result is compared to a rule criterion that represents the worst case tolerable fume toxicity stipulated by regulations or otherwise. The ranking and comparison of different hazard potentials that would otherwise remain unwieldy is rendered tractable by the common format of the RFT notation.

The RFT rules utilized within the industry yield disparate rankings, rather than focusing on a reliable unique result, raising questions about their worthiness as hazard potentials. This irregularity remains a foremost issue within this report, illustrated with fume results from instrumented shots and thermodynamic reaction chemistry code TDRC. The work principle from thermodynamics restricted by a chosen constraint is utilized for theoretical fume resolution rather than the more traditional hydrodynamic detonation theory. This circumvents a recognized difficulty related to the nonideal detonation reaction characteristics of typical mining explosives. Tabulated discrepancies from the different RFT rules typically outweigh the uncertainty in fume component concentrations, regardless of the type of resolving method used. The untrained or unwary worker can misinterpret and rely upon the formulated nature of the RFT rankings, without questioning their limitations, and thereby gravely underestimate the real fume toxicity. In underground mines, where fume dilution is naturally restricted, such misjudgments in respiratory hazards can invite unwarranted risks. Workers who reflect upon this report's observations will hopefully remain wary of weaknesses in the formulated RFT hazard potentials, gain a wider perspective, raise work site questions, and make resolutions to work under safer conditions.

INTRODUCTION

Warnings related to the hazards of toxic fumes are found in reference books of the explosive industry [1,2,3,4]. The undiluted fumes just after an explosive blast are relatively concentrated, rather toxic and therefore quite harmful. For underground shots, the semi-trapped working space restricts the rate at which natural dilution and forced ventilation reduce the toxic fume concentration. Nonhazardous conditions have not always prevailed when work was resumed, resulting in serious or fatal incidents in underground operations [5]. Workers have returned to the blast scene without waiting the time required to reestablish nonharmful working conditions, indicating that some miners have an improper understanding of the nature and quantity of toxic fumes resulting from the detonation of commonly used commercial explosives [3]. Threshold toxicity restrictions for a nominal workday and other noted information are utilized in conjunction with a rudimentary ventilation model to resolve typical waiting times needed to restore nonharmful working conditions.

Recently a novel constraint theory was formulated for resolving the work principle of traditional thermodynamics, yielding the remnant (close to last) equilibrium state for numeric code TDRC to predict the fume spectrum for mining explosives undergoing nonideal detonation [6]. No rationale for utilizing the nontrajectory work principle of thermodynamics rather than the traditional hydrodynamic theory of Zeldovich von Neumann Doering ZND is offered, except to note that the latter remains questionable for nonideal detonation without some readjustment. Rough comparisons from the unfinished (unrefined) nontrajectory work principle with a number of reported mine shots is relegated to the noted reference, though the tentative fit is respectable [6]. The hazard potentials taken as RFT results are predominately determined by the stable fume components, which is fortuitous, since the unstable fume components require shots with time dynamic instrumentation or the resolution of nonequilibrium rate kinetics in conjunction with the work principle technique [6].

Within this report, the hazard potentials are reformulated as results from RFT-X rules with uniform notation and units rather than the traditional formats that otherwise are found in different regulations, guidelines and handbooks. The RFT rules work only with the restricted set or tally of component concentrations in their respective formula. The tag X relates to the formula's origin or role and distinguishes the different rules. Rule results for a chosen fume spectrum are compared to their respective RFT criterion, the worst case tolerable toxicity, without restriction or regard for the type of charge formulation that originally yielded the fumes. Recognition is taken that none of the current RFT rules incorporate hydrogen cyanide HCN, indicating that the tally normally remains incomplete when compared to recognized possibly occurring toxic components.

Though the RFT rules are utilized to yield toxic hazard indications and understand risks. the RFT comparisons do not remove or replace the requirements or conditions set forth by relevant regulations or guidelines. For regulation testing, candidate explosives fail when the RFT results exceed their criterion, thereby denying their usage under the relevant mining conditions. Unfortunately, some of the traditional guidelines represented by the RFT rules that remain within the mining industry cast a tremendous shadow. Regulations or guidelines invoke RFT ranking tests to reduce or limit the range of toxic problems, which ought not to be interpreted as rendering either complete or useful measure of the toxicity hazards. Reversion to the older indicators as sole ranking criteria clouds the risk issue because the unweighted relationships are restricted in form and can noticeably underestimate the risk of hazards. Workers need to remain wary of such circumstances for there are numerous and unexpected influences that govern the formation of dangerous fumes.

Toxicity Mechanisms Underlying Fume Hazards

Traditionally the terminology fumes and smoke refer to the poisonous and nontoxic portion of the reaction gases respectively. Within this report, the terminology fume spectrum refers to the tabulated concentrations of reaction gases regardless of their nature, transformed to standard reference conditions of 25 °C and one atmosphere. When referring to the RFT restricted tally of components, the notion fume spectrum still remains useful whether or not the disregarded portions have negligible or noteworthy toxicity. The RFT formulas incorporate only concentrations of molecular species except for the unweighted mixture of nitrogen oxides $NOX = NO + NO_2$, where nitric oxide NO is colorless and nitrogen dioxide NO_2 is rusty brown. When the traditional ranking technique does not resolve the two NOX components, the RFT rules utilize NOX; otherwise, the two resolved components are taken.

The two fume spectrum components that tend to dominate the relative fume toxicity RFT results are CO and NOX. Historically CO received the major focus due to a relatively high rate of incidents, but more recently the concern has risen over NOX. This shift in wariness has resulted from the deployment of different types of charge formulations within the mining industry and from a reevaluation of the techniques used for ranking the hazardous nature of toxic fumes. NOX is extremely dangerous because of its insidious nature, granting the worker little warning, when inhalation fails to set up defensive respiratory reflexes [7]. Typical of circumstances was a workman who inhaled dynamite fumes for some time, felt well during the working day, noticing no ill effects that night, only to die the next day of pulmonary edema [8]. Nonfatal exposure to NOX is just as treacherous, rendering tissue damage with reduced recovery for stronger concentrations. NOX was often taken as NO_2, since NO is relatively unstable in the presence of moisture and oxygen. The transforming reactions are however somewhat sluggish and with dynamic instrumentation notable proportions of both are detected in mine fumes [9,10].

Nonsmoky transparent atmospheres are not necessarily safe, for CO is nonirritating, without color, taste, or odor. Regarded as an asphyxiant, it was originally thought to work by replacing or displacing the oxygen transported by the hemoglobin [7,8]. In a recent interpretation, the hemoglobin is noted to work by cycling between two states or conformations, denoted R and T [11]. Carbon monoxide poisoning works by locking the hemoglobin molecules into the R-state, shunning the T-state, and thereby impairing the ability of the hemoglobin to release oxygen in the tissues. The references discuss the other toxic components in the RFT formulas, though their role usually tends to be minor for RFT tabulations because of their relatively smaller concentrations [7,8].

Traditional and Recent Underground RFT Rules

The reference name for role or origin, the RFT tag, the formula rules and their criterion are noted in the columns of Table 1 respectively. The formula concentrations designated by bracket terms are fume component volumes per unit explosive mass, taken at standard reference conditions. The last column information represents unit conversions, except for the fume class criteria, which would not transform as wanted without stipulating the cartridge mass. For cartridges of the requisite dimensions, the mass is roughly 200 grams, yielding the rounded off tabulated results. The relative fume toxicity rule for recent US permissibility regulations governing underground coal mining, RFT-P, utilizes constant multipliers to yield the CO concentration that renders equivalent toxicity. The historic Russian formula RFT-R is the widely recognized forerunner of such weighted rules, with a constant nonunity multiplier in recognition that harmful influences vary with the toxic fume composition [9]. Technically the NOX multiplier could not be represented as a constant and also render equivalent toxicity which would make it a function of the ratio of nitrogen oxides in the NOX mixture. For candidate testing, the Russian criterion 50-cc/g in relation to results from the RFT formula would normally be more stringent than its counterpart comparisons with the US 156-cc/g criterion [12,13]. Though the Russian rule was not rigorously constructed to render equivalent toxicity, it is more tractable to implement, requires fewer and less difficult types of measurements.

Table 1. 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

The formula rules for ranking Fume Class RFT-C or RFT-C` and the older US rule for permissibility regulations RFT-U are just resultant sums of unweighted concentrations. Without utilizing multiplying constants, they are unable to reflect the differential toxicity within their tally of components, and they underestimate the CO concentration that would render equivalent toxicity [14]. The references reveal some confusion regarding the requisite tally of toxic components for Fume Class. The tally of one reference has hydrogen sulfide H_2S, CO and NOX [3]; the tally in the second reference skips NOX [15]; and the third reference remains noncommittal, without a tally [2]. The range of tractable possibilities is represented by the two formulas RFT-C and RFT-C`, where RFT-C includes CO and $H_2S$ without the NOX, while RFT-C` includes the NOX. Notice that RFT-U would equal those for RFT-C` for tabulated numerical results with zero or negligible H_2S in the fume spectrum.

WEIGHTING OR MULTIPLICATION CONSTANTS

The RFT-P rule was formulated to render equivalent CO toxicity using the multiplying constants noted in the last column of Table 2. The other columns respectively show the name, molecular formula, and threshold level value TLV time weighted average TWA [16].

The reciprocal ratio of the relevant component TLV–TWA to that for carbon monoxide CO yields the relevant multiplication constants. Recently the TLV-TWA of carbon monoxide was reduced from 50 ppm to 25 ppm (with *), which would double the CO multiplier [17]. Technically the tabulated multiplication constants would be renormalized so the CO constant remains unity, halving the other constants and justifying an identical reduction in the rule criterion. These readjustments are not incorporated into the regulations or guidelines or their corresponding RFT, and therefore are not pursued here, except to later note a worthwhile readjustment in the waiting time required for restoring nonhazardous work conditions.

Table 2: Multiplying Weights For Toxic Fume Components

Toxic Gas	Molecular Formula	TLV – TWA [ppm]	Numeric Multiplier
Carbon Dioxide	CO_2	5000	1/100
Carbon Monoxide	CO	50(25*)	1(2*)
Nitric Oxide	NO	25	2
Nitrogen Dioxide	NO_2	3	17
Ammonia	NH_3	25	2
Hydrogen Sulfide	H_2S	10	5
Sulfur Dioxide	SO_2	2	25

Working with the older renormalization (without *), the fume component concentration times its multiplier yields the CO concentration that renders equivalent toxicity for just that component, with the resultant influence found by summing over the tally. This numerical technique provides a working (operational) definition of carbon monoxide equivalent toxicity resolved for threshold concentrations, with rule usage regarded as worthwhile at other conditions. Though using this toxicity rule for hazardous circumstances far removed from threshold conditions could be questioned, it is the marginal circumstances near threshold that normally warrant interest. None of the other RFT rules render the CO concentration for equivalent toxicity when the relevant nonhazardous threshold concentrations are installed in their formulas. For non-regulation purposes, the RFT formula could be revised to incorporate other toxic components, with the multiplication constants formed with reciprocal TLV-TWA ratios.

Mining Usage Influences and Fume Tests

The quantity and nature of toxic fumes are governed by numerous conditions: type or grade of charge formulation, mixture uniformity, hole contaminates, water resistance, marginal initiation, stratum confinement, rock hardness, dust interactions, and other conditions of usage [1,2,9,18]. The rock or stratum surrounding the charge regulates the work output, reducing the rate of fume expansion, partially trapping the reaction products, and permitting slower reactions to transpire that would otherwise remain incomplete. Hole-to-hole wave interaction can partially desensitize the charge formulation, resulting in shifted reaction kinetics and weaker detonation rates [19,20]. Under the rift compression (heave forces), some reaction gases are forcefully driven into the cracks and pores of the roof, walls and floor. Fumes trapped within the stratum and dust can be released back into the working environment [18].

Fume Class rankings depend upon the quantity of poisonous gases released, traditionally called fumes, when an explosive cartridge is detonated under test conditions in the Bichel Gauge [2,3]. For permissibility testing, the Crawshaw Jones Fixture was also used [21]. The output rate and work done on the rigid cannon wall differs somewhat from that of a more compressible stratum. It noteworthy that carbon oxides tend to rise with rigid hard rock confinements while conversely the nitrogen oxides tend to rise in cracked or friable rock conditions.[22] Revision of the regulations transpired as a result of substantial research, involving comparison with mine shots [23]. Thereupon the Large Gallery Chamber Test replaced the former two fixtures for ranking toxic fumes of permissible candidates [10].

Traditional testing techniques for the determination of toxic fumes from cap-sensitive type explosives would not work for blasting agents, which require larger charge diameters and total masses to shoot properly and render typical (in situ) fumes. Recently an underground facility for detonating confined charges within a controlled volume was developed [24]. The NIOSH underground fumes facility for toxic fume measurements has a 274-m^3 chamber, 324-kg air within the walls [24]. The mining explosive under test has a typical mass of 4.54 kg and is confined by a 10.2-cm diameter cylindrical steel pipe for proper detonation. Except for the rupture and fragmentation of the cylinder, the explosive works upon and transfers heat to the air reservoir within the chamber, while interacting only weakly with the walls or the other chamber structures.

TROUBLES WITH TRADITIONAL ZND AND NONEQUILIBRIUM

The reaction of mining explosives is quite nonideal, and not reconcilable with the traditional requirements of the Zeldovich von Neumann Doering ZND theory of detonation [25,26]. For the traditional ZND theory, the reaction thermicity in the referenced relation must vanish for the Chapman Jouguet CJ sonic condition. Nonideal explosives undergo reaction through the narrow transonic region, so the zero thermicity requirement is a recognized conflict. This difficulty can be rendered moot by incorporating a representative loss term in the theoretical formulation, so the relevant relationships remain numerically bounded [27]. The resolution raises questions regarding the reaction process undertaken, yielding philosophical room for using the work principle from thermodynamics [28,29].

For rock mining or fume testing, the restoring influences that try to uphold mechanical and thermal equilibrium rapidly widen the fume zone within the reservoir, via Le Châterlier's principle [30]. Under the transitory circumstances with declining zone temperatures, the restorative influences that try to maintain chemical equilibrium falter, so that total equilibrium remains plausible only while the fume zone stays thermally hot, keeping chemical relaxation times ultra small. With cooler temperatures, the relaxation times grow drastically, precipitating out-of-equilibrium circumstances within the working fluid. Wall or dust interactions and some residual nonequilibrium reactions persist noticeably at the cooler temperatures within the underground chamber at the hour of measurement, ruining the presumption of terminated reactions. Thermodynamic reaction chemistry codes TDRC yield results that require total equilibrium conditions for the working fluid and they would be quite inappropriate for resolving the nonequilibrium (Q*-point) measurement state. Questions arise regarding a former state that was the last respectable remnant of total equilibrium, and therefore worthy of fume spectrum resolution with TDRC.

Numerical resolution of the reactive fluid dynamic equations can resolve the reaction zone with time graphics and probe the workings of nonideal and unstable mechanisms [31]. Nonequilibrium conditions tend to remain rather intractable for the hydrodynamic (trajectory) techniques, so the reaction components are usually reckoned as frozen for chosen temperatures on the late stage (post CJ) trajectory. Historically TDRC represented the relationships for reacting matter in dense states with fugacity type terms [32], though recent codes use the numerical minimization of thermodynamic potentials. Notable disagreement remains between theoretical codes renowned for their questionable constants and representations of matter, test fixtures renown for their rigged conditions, and field measurements renown for their poor reproducibility [1,4,10,19,31]. Numerical fume spectrum results tracked downward on some trajectory from the high density region could be wrong or unreliable, if the equation-of-state (EOS) formula constants are reckoned badly, yielding results that are undesirable for ranking fume toxicity. The work principle can not be tampered with or remedied in this fashion, which could be regarded as a disadvantage or a useful circumstance.

WORK PRINCIPLE FOR PREDICTING TOXIC FUMES

The work principle method 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' terminal (key) states. The work principle resolution utilizes a quasi-potential or negative work function, with numeric results requiring some appropriate thermodynamic reaction chemistry code TDRC. The underlying method is unable to restrict reactions, tailor the work output or otherwise resolve states within the trajectory transitions, so that the trajectory terminology is worthwhile only in a figurative or rough sense. The work principle incorporates a working fluid that interacts irreversibly with a tremendous reservoir or reversibly upon a mechanical agent. When modeling underground fume tests rather than rock blasting or other circumstances, the working fluid represents the reaction ingredients undergoing transformation to resulting products, the reservoir represents the underground chamber walls and reservoir of air, and the mechanical agent remains an uncorrelated item [6].

Within the underground test chamber, the declining temperature within the widening fume zone reduces the reaction rates, resulting in out-of-equilibrium circumstances for the Q*-state, representing the measurement conditions. 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 energy constraint. Though hydrodynamic ZND type techniques require complex equation-of-state EOS for the whole trajectory, the work principle formulation requires an EOS that works just for resolving the terminal state.

With the zero-net-interaction trapping constraint, the resulting Z-state is a thermally hot and rarefied state, reconcilable with the ideal gas domain. Under the circumstances, the TDRC chosen for resolving the fumes was the NASA Lewis Complex Chemical Equilibrium Code, which works for ideal condensed phases and gas mixtures [33].

The work principle makes it hard to remedy or to tamper with the resulting Z-point fumes: trajectory readjustment or instituting frozen reactions is forsaken and trajectory terminal states are results rather than stipulations. Resetting the EOS formula or constants would also be rendered ineffectual. Though the nonequilibrium transition still remains unresolved, it is noteworthy that the work principle rigidly fixes the relevant jump Z—Q*, reducing the uncertainty for modeling the transitory reaction rate kinetics. Though further refinements are under development, Z-point fume results remain useful for illustrating the minimum resolving capacity of the work principle formulation and for rendering tolerable fume spectra utilized for the RFT comparisons.

THERMODYNAMIC THEORY UNDERLYING WORK PRINCIPLE

The work principle formulation remains tractable regardless of the process undertaken with the relationship retaining the ubiquitous inequality that formally characterizes traditional thermodynamics or its more recent interpretation referred to as statistical physics [34,35]. The work principle model utilizes a composite system of three interacting components that otherwise remain isolated from the rest of the universe and therefore governed by the laws of thermodynamics. The working fluid can have reactive composition, transfer heat to or work upon the reservoir or work upon the mechanical agent in a reversible nonexpansion way. The reservoir must retain constant thermal mechanical characteristics and therefore have tremendous (mass) proportions compared to those of the other two components, and it is unable to interact directly with the mechanical agent. None of the components interchange particles so the working fluid mass remains constant. The resolution technique utilizes constraints that work chronologically, though they are not required to formulate the work principle itself.

The work principle requirement incorporates a quasi-potential Y_Q or negative work function $[-W_F]$, written per unit working fluid mass since the TDRC render their numeric results that way. The work function and quasi-potential terminology tends to be redundant though useful. They are defined by the relationship:

$$-W_F \equiv Y_Q \equiv \left[U - T_R \cdot S + {}^{P_R}\!/_{\rho} \right]$$

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 (or Rho). Neither the quasi-potential nor the work function qualifies as a working fluid state function since they depend upon reservoir characteristics, temperature T_R and pressure P_R, despite their requisite constancy.[36] The resulting construction of the quasi-potential, represented as a superposition of working fluid state functions with constant reservoir multipliers, is trajectory pathway independent, regardless of process irreversibility or nonequilibrium, and therefore has formidable theoretical capacity. The work principle inequality relation taken from the noted references [34,35] is then

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

The **Work** term represents the work done by the working fluid upon the mechanical agent, for the type of process rendered: reversible takes the equality and irreversible takes the inequality. The work done upon the mechanical agent would equal the work function rise ΔW_F or $\Delta[-Y_Q]$ for a reversible path. Restoration work refers to the work rendered by (not upon) the mechanical agent to return the working fluid to the original state in a reversible way. Noting the restoration work required is a way to recognize the system's propensity for chemical reaction work [37]. To render a macroscopic (finite) reversible transition requires an infinite number of quasi-static (infinitesimal) steps and would normally take forever.

When a closed cycle integration regardless of trajectory is taken over the former relationship, the W_F or Y_Q terms yield zero net results since the work function or quasi-potential registers transitions like state functions, yielding zero differences upon returning to their original values. The resulting work done upon the mechanical agent over the whole cycle would be zero or negative, **Work** ≤ 0. regardless of the thermodynamic process undertaken. Therefore, the mechanical agent would have to render the restoration work without ever taking recourse to the reverse possibility, forever forbidding the prospect of a perpetual motion machine.

It is worthwhile to invoke the terminology that natural processes refer to macroscopic (finite) transitions with some irreversibility, however slight. Reversible infinitesimal fluctuations would take finite time and are therefore not excluded, though they can not wholly account for natural process. For work with toxic fumes, only natural processes with zero net **Work** are considered, as though the mechanical agent was dysfunctional. Technically the mechanical agent is not removed from the work principle model, just rendered moot, so no device in the reaction process or underground fumes chamber needs be identified with it. With the zero net **Work** restriction, the work principle relation reduces to

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

Without the mechanical agent to render restoration work, returning to the starting state upon undergoing a natural process is impossible. Restoration work remains an illusion that requires a reversible process taken in reverse time travel (or reverse 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 thermodynamic trajectory motion. The Y_Q partial derivatives with respect to the unrestrained χ, while holding κ constant, are utilized to form the constraint representation with the thermal or mechanical state variables. The unrestrained infinitesimal change $\delta\chi$ taken while holding κ constant would remain otherwise 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 understood [38].

$$\delta\left[-W_F\right]\Big|_\kappa \equiv \delta Y_Q\Big|_\kappa \equiv \sum\nolimits^{`} \frac{(\delta\chi)^J}{J!}\cdot\frac{\partial^J Y_Q}{\partial\chi^J}\bigg|_\kappa \le 0$$

Technically the subscripts should bear witness to the restriction of chemical equilibrium, though that requirement is universally presumed for the terminal state resolution, so the reduced notation of just displaying κ the thermal mechanical constraint is tractable. Retention of only the lower order J terms is required for resolving and interpreting infinitesimal transformations, as noted by the grave accent on the summation. For resolving the minimum trapping state, the first derivative $\partial Y_Q/\partial\chi\,|\,\kappa$ would reduce to zero for the terminal state, while the second order derivative $\partial^2 Y_Q/\partial\chi^2\,|\,\kappa$ would be positive for the trajectory trapping minimum. The multiplication of the nonzero unrestrained $\delta\chi\cdot\delta\chi$ with a positive $\partial^2 Y_Q/\partial\chi^2\,|\,\kappa$ yields the wrong sign for the inequality relation. The only workable solution would require that the unrestrained $\delta\chi$ vanish, which represents stalled trajectory motion, until the constraint is replaced with a different restriction or thereupon is left unrestrained to travel 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 principle [39]. Uncertainty principles render trajectory notions obsolete and force worst case minimum tolerances on canonically conjugate variables. When multiplying the uncertainty tolerances for the canonical coordinates, the multiplication result in quantum mechanics has units of Planck's constant (or action), while the multiplication result in thermodynamics has units of Boltzmann's constant (or entropy). 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. It is worth noting perhaps that the nontrajectory work principle tends to operate functionally like quantum mechanics, with terminal states rendered as the result of recognized or tractable operations, while the nonequilibrium states within the transitions remain unresolved.

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_I of the original and unreacted thermodynamic state. During transitions nontrivial influence is possible since the work done upon or heat transfer with the reservoir is unrestricted except for registering the zero net energy change for the overall macroscopic process. With reservoir interaction, no overt restriction regulates the working fluid's entropy change. Instead transformations that yield a reduction in the quasi-potential can occur, while the reverse inequality conditions that violate the reduction of the quasi-potential Y_Q are forbidden. The restriction on the terminal trajectory is written $U = \kappa$ for theoretical resolution, with $\kappa = U_I$ for the numerical resolution using the relevant TDRC. Utilizing hindsight, the forthcoming results were reduced in form by defining the K-function 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 $K_R \equiv P_R/R^*T_R \equiv 40.874$ µmol/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 $\chi = S$ or $\chi = y$ respectively,

$$\delta[-W_F]\Big]_U \equiv \delta Y_Q\Big|_U = (-T_R)\cdot\delta S\cdot\left[1-\frac{K_R}{K}\right] = \left(\frac{T_R W}{T}\right)\cdot\delta y\cdot\left[1-\frac{K_R}{K}\right] \le 0$$

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 must rise (fall) and the density 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 such results are worthwhile only if the chosen TDRC and related EOS characterize the working fluid in the thermodynamic domain under investigation.

When the zero net interaction Z-point 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-point 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-point 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.

NUMERICAL ILLUSTRATIONS AND COMPARISONS

Fume concentrations were transformed to standard reference conditions so that reported fume information would not reflect the irregular working conditions and follow the normal criterion rankings techniques. Large Gallery fume results for pulverized ANFO mixtures in the density range 0.74 or 0.75 g/cc were formerly reported and noted in Table 3 with converted units [40]. The columns respectively show the shot number, fuel oil fraction, mixture density, concentrations [cc/g] of CO_2, CO, NO, NO_2, NOX and measured detonation rate. The NH_3, H_2S, and SO_2 were not reported and were regarded as negligible in any RFT rule requiring those concentrations.

Table 3. Reported Fume Spectrum Q*-State Results

Shot Num.	Fuel Oil [%]	Density [g/cc]	CO_2 [cc/g]	CO [cc/g]	NO [cc/g]	NO_2 [cc/g]	NOX [cc/g]	Det. Rate [mm/µs]
#25	2	0.75	40	2	7	9	16	3.2
#30	3	0.74	57	5	7	6	13	3.4
#18	4	0.74	85	7	6	1	7	3.3
#27	6	0.75	90	9	1	~0	1	3.6

The Z-state results in Table 4 represent a transient equilibrium state under constraint while Q* represents a transient nonequilibrium state at the time of measurement. The unrefined work principle theory will not yield the nonequilibrium Q* results, so only the rather stable Z-state fume components CO_2, CO and NOX were recorded in Table 4 as tentatively representing Q* results within the hour of measurement. Without and with RAX (air ingestion) results [6] were rounded to the closest [cc/g] and they can resolve all but one of the RFT rules. For the rule exception RFT-P, it is recognized that the Z-state NOX transforms rapidly so roughly half is NO and half is NO_2, yielding the remaining concentrations for working out the Q*-state tally.

Table 4. Numeric Fume Spectrum Z-state Results

		Without Air Ingestion			With Air Ingestion		
Shot Num	Fuel Oil [%]	CO_2 [cc/g]	CO [cc/g]	NOX [cc/g]	CO_2 [cc/g]	CO [cc/g]	NOX [cc/g]
{#4}	4	68	3	5	68	3	5
{#5}	5	79	9	4	79	9	4
{#6}	6	84	21	3	89	16	4
{#7}	7	83	40	1	104	19	5

The reported formulations were obviously not stoichiometric, but that is not a requirement of utilized or candidate charge formulations. The relative fume toxicity values deduced from the different formulations and RFT rules were rounded off as shown in the middle four columns of Table 5. The uncertainty in the last column was taken as twice the relative deviation [for (+/-)], which was defined as the standard deviation divided by the mean. Notice the wide range of hazardous potentials represented by the different RFT rules.

When compared with their respective criterion, the tabulated RFT results determine whether the (illustration) candidate charge formulation remains tolerable or the toxicity is too hazardous. The rows with RFT-C results over 23 cc/g, RFT-R results over 50 cc/g, or RFT-U or RFT-P results over 156 cc/g would fail the corresponding test. For the instrumented shots only charge formulation #27 passed all the tests, while for the theoretical computations only the formulation #7 failed some test. The RFT-C` formula is unorthodox within the US and was not included. The recent rule for permissibility is more restrictive than the older rule as was reported theoretically and recognized by comparisons in Table 5; notice the RFT-P results are higher than RFT-U results though the criterion remains unchanged. The Russian rule criterion relationship tends to be rather stringent with respect to noxious fumes from candidate explosives, as noted by the greater number of unacceptable circumstances. The tradeoff noted later for the more restrictive Russian criterion is the reduction of the total refresh work required to restore nonharmful working conditions, which for the miners can translate into shorter waiting times until safely resuming work.

Table 5. Relative Fume Toxicity RFT for Different Rules

Theoretical Z-Q* Results, Without and With Air Ingestion

Numeric or Shot Result	RFT-C [cc/g]		RFT-U or RFT-C`		RFT-P [cc/g]		RFT-R [cc/g]		Uncertainty In RFT [%]	
#25	2		18		169		106		212	
#30	5		18		122		90		192	
#18	7		14		37		53		152	
#27	9		10		12		16		53	
{#4}	3	3	8	8	51	51	36	36	187	187
{#5}	9	9	13	13	48	48	35	35	140	140
{#6}	21	16	24	20	50	55	41	42	82	111
{#7}	40	19	41	24	50	68	47	52	22	114

RESTORATION OF NONHAZARDOUS WORK CONDITIONS

Regulations for underground coal mines stipulate requirements for quality and quantity of the refresh air sufficient to dilute, render harmless, and remove reactive, noxious and harmful gases, dust, smoke and fumes [41]. For bituminous and lignite mines the minimum flow rate reaching the working face is 1.42 m^3/s, while for anthracite coal mines, the requirement is 0.71 m^3/s, written in metric units. The regulations for underground coal mining require that workers not return until the blast area is clear of smoke and dust and properly inspected for misfires, methane, and other hazardous conditions [42]. The roles of the RFT rules and criterion warrants discussion in regards to the time miners should wait for dilution and removal processes do their work and render harmless the hazardous conditions of toxic fumes. Without irregular charge performance, the toxic concentration remains under the RFT criterion; otherwise the charge formulation would presumably have failed candidacy testing. The worst case tolerable concentration, the RFT criterion, is utilized to resolve the refresh conditions in underground work sites because logically the charge formulation toxicity can reach the worst case. A quite rudimentary though tractable model is discussed next to illustrate trends, though it should not replace specific work site computations done by trained personnel.

In our rudimentary model, the toxic molar concentration $\chi(t)$ at time t that renders CO equivalent toxicity is utilized. This reduces the complications of uncertain influence related to the particular nature or mixture of toxic fume components. The work zone of constant size like a chamber or bratticed off region where toxic fumes are waylaid or trapped is referred to as the 'room'. The ratio of total charge mass to room size is referred to as the trapping density. For the Underground Fumes Chamber the charge mass is typically 4.54 kg and the room size is 274 m^3 yielding a trapping density 17 g/m^3. For the Large Gallery, the trapping density is 12 g/m^3. For underground measurements without rigid chambers a rough number for the original fume concentration would be under 1% or the zone would rapidly widen from the wind rushing to restore the ambient pressure. Noting that $\chi(0) = RFT_C \cdot \rho_T$, with RFT criterion of 156 cc/g and $\chi(0)$ of 1% concentration would yield a trapping density ρ_T of 64 g/m^3. The reduction of toxicity to the nonharmful working condition denoted $\chi_C \equiv \chi(t_C)$ requires a waiting time t_C. The nonharmful work condition $\chi_C = 50$ ppm for the TLV-TWA of CO in Table 2 is taken as the reference case, with the recent revision taken later as a trend readjustment.

The room is refreshed with nontoxic air and the resultant toxic mixture is removed from the room at a constant rate, Q`, thereby diminishing the toxicity, within the room. Therein the toxic fumes are assumed to redistribute themselves, forming $\chi(t)$ a uniform non-constant toxic concentration. Wall losses, dust interactions or further fume reactions are disregarded. Fluid conservation relations with constant Q` yield a tractable relationship that can be resolved for the waiting time t_C, which is required for the refresh rate to reduce $\chi(0) \equiv \chi_O = RFT_C \cdot \rho_T$ to the nonharmful working conditions, $\chi_C \equiv \chi(t_C)$.

$$\textbf{Wait-Time} = t_C = T_{RC} \cdot \mathrm{Log}\,[\chi_O / \chi_C]$$

$$\textbf{Where, } \chi_O = RFT_C \cdot \rho_T,$$

$$\textbf{Where, } T_{RC} \equiv M_X / [\rho_T \cdot Q`].$$

The collection of constants T_{RC} multiplying the natural logarithmic function represents the natural relaxation time. For underground shots with 15 holes and 1.36 kg/hole, the total mass charge M_X would be 20.4 kg. The room size, M_X / ρ_T, would remain proportional to the charge mass for constant trapping density. The same charge mass M_X, 20.4 kg, and RFT criterion, 156 cc/g, are utilized to illustrate results in Table 7. Respectively, the columns show the requisite circumstance, the trapping density, initial concentration, the flow rate, and the resulting waiting times rounded up to the closest quarter hour when in hours. Transformation to consistent units is required.

The graph in Figure 1 shows the trends in waiting times to restore nonharmful working conditions versus the trapping density. The readjustments for the other trends with respect to the reference case are noted in Figure 2, with results for the trend maximum waiting times. Reducing the nonhazardous threshold from 50 to 25 ppm increases the waiting time, while reducing the RFT criterion or raising Q` the flow rate decreases the waiting time. When the Russian criterion replaces the US criterion, recognition should be taken that more noxious formulations that formerly passed candidacy would fail but that the tolerable remainder could be utilized with shorter waiting times. The RFT criterion readjustment is recognized as a tradeoff between restrictions on the candidate explosives and the refresh work necessary to restore nonharmful working conditions.

Table 7. Waiting Times for Model Results

Trapping Density Equivalent Circumstance	Trapping Density ρ_T, [g/m^3]	Initial Toxic Concentration, $\chi(0)$	Flow Rate Q [m^3/s]	Waiting Time t_C
Room Size For $\chi(0) = 1\%$	64	1.00%	0.71	40 min
			1.42	20 min
Fumes Chamber Underground Mine	17	0.27%	0.71	2 hr
			1.42	1 hr
The Large Chamber	12	0.19%	0.71	2½ hr
			1.42	1¼ hr

The waiting times resolved were not small, suggesting that rushing back to the work face could be tantamount to reducing rather narrow safety margins, or reentering unsafe conditions, perhaps revealing why toxic fumes still cause fatal and nonfatal incidents. Naturally readjustments, such as raising the flow rate, could be taken to reduce the waiting time. Recall now however that our model presumes no irregular reactions, so an outstanding question remains. Would those readjustments then yield enough safety margin at work sites if the charges function poorly (malfunction), releasing shifted fumes that could have double or quadruple their usual fume toxicity[43]?

CONCLUSIONS AND RECOMMENDATIONS

The rule notation that renders hazard potentials taken as relative fume toxicity RFT results worked rather well, permitting the type of rankings and comparisons that would otherwise hardly be considered. The widely dispersed RFT results for the different rules, noted in Table 5, revealed high uncertainty, rather than focusing on a unique number, worthy of being a hazard potential. The underlying rationale is quite simple, some of the RFT rules ignore toxic fume components that are not negligible, or fail to weight them in proportion to their recognized toxicity. Numerical results for unweighted rules tend to underestimate the CO concentration that renders equivalent toxicity. The ramifications from utilizing traditional rules and reported fume concentrations from a given charge formulation demonstrate quite clearly the okay-not-okay nature of the different RFT hazard potentials. Regulations and guidelines relate to the relative fume toxicity, among other things, and unwary workers reflecting only upon those criteria rather than understanding the true nature of the rules and their limitations, could readily underestimate the hazardous nature of the toxic fumes from their explosives.

The work principle technique with the TDRC from NASA was utilized to render the fume spectrum results for the numerical illustration, revealing a range of uncertainties similar to that found for the reported instrumented shots. The Russian rule yielded a noticeable number of unacceptable results compared to those computed from the US rules in the illustrations undertaken. The recent RFT-P rule results tended toward intolerance more than their older RFT-U counterparts despite their common criterion, reinforcing the notion that the weighted rules are more stringent. No recognition or comparison was made for toxic components not registered in the RFT-P tally, though the reciprocal ratio technique that formed the rule could be utilized to raise the tally of wanted toxic components, refining the relationship for rendering equivalent CO toxicity.

The trends in waiting times to restore nonharmful working conditions noted in Figure 1 were resolved for a chosen reference condition and several other circumstances, yielding nominal results of a few hours, with maximum times under one day. Despite our rudimentary ventilation model, trained persons ought to be consulted regarding the waiting times until nonharmful working conditions are restored at their work sites. Hopefully those persons responsible for transferring or utilizing relative toxicity information will reflect upon the observations made here, remain wary of the rules and their limitations, gain a wider perspective by raising work site questions and when necessary implement safer mining procedures. The possibility of utilizing remote or portable instrumentation to monitor or detect multi-component toxic fumes should not be overlooked.

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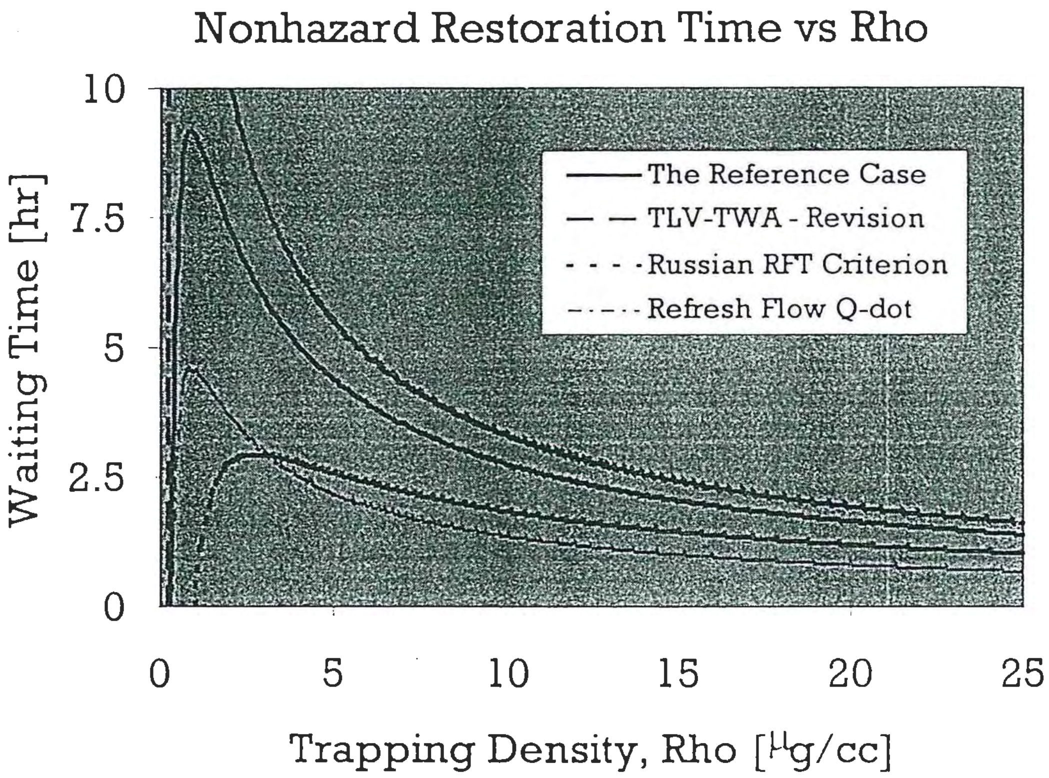

Figure 1. Graph Of Waiting Time for the Restoration of Non-Hazardous Working Conditions [hr] versus Trapping Density, Rho [μg/cc].

Table 7. Relevant Information for Waiting Time Trends

Readjustment To Reference Case	Threshold For Non-Hazardous	RFT Rule Criterion	Flow Rate Q-dot	Trapping Density for Max.	Waiting Time Maximum
	[ppm]	[cc/g]	[m^3/s]	[μg/cc]	[hr]
None	50	156	0.71	0.871	9.17
TLV-TWA	25	156	0.71	0.436	18.35
Russian Criterion	50	50	0.71	2.72	2.94
Q-dot Flow	50	156	1.42	0.871	4.59

Figure 2. Relevant Information for the Four Graphical Trends of Waiting-Time versus Trapping Density, Rho [μg/cc] or [g/m^3].

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