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## Table of Content

Flame, detonation, explosion – when, where and how they occur *(plenary lecture)*  
*Michael Liberman* .................................................................................................................. 5

Temperature Measurement for Meeting the EU Directive on Waste Incineration  
*Elisabet Blom and Dan Loyd* ................................................................................................ 25

Biomass as an Energy Source: the Challenges and the Path Forward  
*Elinor Bolyos, David Lawrence* ¹ and *Anders Nordin* ........................................................ 27

Environmental and Economic Aspects Concerning the Reuse of Explosives  
*Erik Dahlquist and Emma Nehrenheim* .................................................................................. 35

Explosion and Fire Hazard Assessment  
*Robert Folchi* ...................................................................................................................... 37

Biological Treatment of Sludge Containing Residues of Explosives and Pharmaceuticals  
*Lillemor Gustavsson, Sofie Jönsson and Bert van Bavel* ........................................................ 39

A Mobile Facility for Destruction of Munitions and Explosives  
*Nico van Ham* ......................................................................................................................... 41

Environmental Research on Munition at FOI  
*Joakim Hägvall* ...................................................................................................................... 43

Organic Compounds in Residues from Incineration of MSW and Biofuels  
*Inger Johansson* ..................................................................................................................... 51

Analysis of Organic Nitrogen Compounds and their Transformation in Biologically Treated Sludge from Pharmaceutical and Explosives Industries  
*Sofie Jönsson, Lillemor Gustavsson and Bert van Bavel* ........................................................ 53

Investigation, Mapping, and Location of Dumped Ammunition. A Project of the Swedish Armed Forces  
*Janne Kjellson* ......................................................................................................................... 55

New Training CD ROM Package on Inflammable Materials  
*Stefan Lamnevik* ..................................................................................................................... 59

Soil remediation. An Overview of Existing Technologies  
*Per-Anders Bergman* ............................................................................................................... 63

Fires in Swedish Match Factories in the 1920s Caused by White Phosphorus-contaminated Red Phosphorus  
*Tomas Lundahl* ......................................................................................................................... 65
Energy Recovery from Packaging Waste – the Result of 12 Years’ Standardisation Work
Barbro Maijgren and Stig Pettersson ................................................................................................. 83

Mass Detonation or Recovery – Environmental Impact of Different Ammunition Destruction Methods
Emma Nehrenheim .......................................................................................................................... 89

Destruction of Conventional and Chemical Munitions in a Dynasafe Static Kiln
Johnny Ohlson .................................................................................................................................... 95

Creativity – a Powerful Tool in Creating New Order from Chaos. A Brief Retrospect of Alfred Nobel’s Ideas and Inventions
Hans Eriksson ...................................................................................................................................... 97

Remediation of Mercury-polluted Sediments through Deep-freezing
Susanne Rostmark and Sven Knutsson ............................................................................................ 99

Risk Analysis and Risk Assessment in the Production of Energy from Waste and Biomass Fuel
Bengt Sahlin ......................................................................................................................................... 101

Temporal Behaviour of Mines and Objects Similar to Mines
Stefan Sjökvist and Dan Loyd ........................................................................................................... 107

Underground Detonation – The Environmental and Safe Process
Arild Skirstad ....................................................................................................................................... 109

Super-critical Fluid Technologies within Chematur Engineering AB
Lars Stenmark ...................................................................................................................................... 111

Testing of Explosives Stability and Remaining Shelf Life of Components in Ammunition Before Recovery, Modernisation, or Demilitarisation
Dennis Taylor ...................................................................................................................................... 113

Addressing Environmental Issues During Acquisition
Ian G. Wallace ...................................................................................................................................... 115

“Excert”, A Europan Pilot Project for Developing and Maintaining Skills and Competence for Personnel in the Explosives Sector
Hans Wallin ......................................................................................................................................... 117

Weapons of Mass Destruction – a Gigantic Disposal Challenge
Kristina Zetterlund ............................................................................................................................ 119
FLAME, DETONATION, EXPLOSION – WHEN, WHERE AND HOW THEY OCCUR
(plenary lecture)

Michael Liberman
Department of Physics, Uppsala University
Box 530, SE-751 21, Uppsala, Sweden

ABSTRACT
Combustion is also involved in explosions for both peaceful and military purposes. In the past decades, there has been a considerable progress in understanding combustion processes and regimes of the combustion propagation. This review focuses solely on explaining various phenomena of premixed combustion: (1) flame propagation, (2) detonation waves, (3) when and how explosions occur, (4) the transition from flame to detonation and (5) when ignition of combustion involves phases of deflagration or detonation. Additionally, the paper will include a discussion of what pollutants are produced during combustion and how clean and efficient combustion can be achieved. Examples of typical combustion scenarios, including flames propagating in tubes, closed chambers or engines are overviewed, along with events of the thermonuclear Supernova.

Results obtained during past decades on the dynamics of flames, the understanding of the nature of burning and mathematical descriptions and numerical modelling of combustion are outlined. I shall talk about such prominent scientists as Yakob Zel’dovich and Lev Landau who were at the origin of modern combustion theory and made fundamental contributions to the understanding of combustion.
1. INTRODUCTION

Combustion is a subject, which is truly interdisciplinary requiring the merging of knowledge in different subjects of physics and chemistry, including hydrodynamics, chemical kinetic, thermodynamics, statistical physics, kinetic theory, and quantum theory. That’s why although combustion has a very long story, which is comparable with the time of human story (we can count at least from the Prometheus time) and great economic and technical impact on almost all sides of human activity, its scientific investigation is of relatively recent origin.

Combustion has a wide variety of uses. Chemical combustion is used for energy production in power plants, gas turbines and engines. Similar process of thermonuclear combustion is a heat source in the Sun and stars. Combustion is also involved in explosions for both industrial and military purposes. Though people are beneficial from using combustion, it however has harmful effects such as unwanted fire, explosions and pollutants and greenhouse effects are produced. Combustion is a process of heat release in exothermal reactions, which accompanied by mass and heat transfer. Combustion can involve all phases of matter – solid, liquid and gas, for example, in solid rocket propellants, liquid droplets burning in diesels, and gaseous combustion in Otto engines.

List of the names of people who made notable contributions in foundation of the combustion science is too long to be given here. These are names of Lavosier, Bunsen, Le Chatelier, Chapman, Jouguet, and many others. I would like to mention names of a great physicists from Russia – Yakov Zel’dovich and Lev Landau, whom I new personally. Virtually all aspects of modern combustion theory bear marks of the names Landau and Zel’dovich. There are many good combustion textbooks, which are aimed at a wide audience from graduate students to scientific researchers and engineers. One of these books written by prominent researchers A. Linan (Spain) and Williams (USA) starts by the following dedication: “To Ya. B. Zel’dovich Who erected the Foundation of the Modern Science of Combustion.”

The principal difficulties in understanding combustion systems are the wide range of time and space scales involved, chemical complexity and multidimensional nature of the flow configuration. In turbulent combustion, the difficulties are further compounded by the complexities of chemical kinetics and the strong non-linear coupling of the turbulence and the chemistry. These turbulence–chemistry interactions arise from the fact that in most combustion systems, mixing processes are not fast compared with rates of chemical reaction and large spatial and temporal variations in species composition and temperature are present. Chemical reaction rates are strongly coupled to molecular diffusion at the smallest scales of the turbulence. Furthermore, the heat release associated with combustion affects the turbulent flow, both from variations in the mean density field and from the effects of local dilatation.

In the face of such difficulties for a direct analytical approach, engineering practice has traditionally resorted to empirical methods for combustor development. While in the last century empirical methods were sufficient for development of combustors, today the marketplace demands much stricter control of pollutant emission and much more effective burning of fuel.

Regimes of combustion and flame dynamics will be of the first priority in this review and we shall not go into details of chemical aspects of the burning process. Realistic burning in a flame may involve up to thousands elementary reactions. Still for a simple estimate most of details of chemical reactions are not important so that some combustion features may be described satisfactory by use of highly idealized model of one simplified irreversible reaction that transfer the fresh fuel mixture into the products of burning. We will also consider here premixed gas combustion, which is the opposite case to diffusion flames. Premixed gas combustion is the combustion of gaseous reactants, which are perfectly premixed prior to
ignition. This implies that all components necessary for the reaction are present in the fuel mixture from the very beginning and in order to initiate reaction one has only to ignite the mixture. Premixed combustion is of practical importance in engines, modern gas turbine and explosions, where the fuel and air are essentially premixed, and combustion occurs by the propagation of a front separating unburned mixture from fully burned mixture. Since premixed combustion is the most fundamental and potential for practical applications, the emphasis will be placed on regimes of premixed combustion and numerical methods for solving the corresponding transport equations.

2. REGIMES OF REACTION WAVES PROPAGATION

The most distinctive feature of premixed combustion is its ability to form a self-sustained reaction wave propagating with a well defined speed, which is either larger or much less than sound velocity. A remarkable feature of premixed combustion is a strong dependence of the chemical reaction rate on temperature expressed by the Arrhenius law for the reaction rate $k = A \exp(-E/RT)$, where $E$ is the activation energy. The activation energy of many reactions is so large, that the reaction rate at the room temperature may be taken zero. On the contrary, increase of the fuel temperature even by a factor 2-3 may lead to the increase of the reaction rate by many orders of magnitude and to a noticeable reaction (Zeldovich et al. 1985). In the case of a strongly exothermic reaction when a considerable energy release is involved, relatively slight increase of the temperature at some region ignites the reaction, which eventually extends over the whole gas.

Two main regimes of combustion should be distinguished: strongly subsonic regime, which is known as a flame, or deflagration, and supersonic regime of the reaction wave propagation known as detonation. In the case of a flame the physical mechanism of flame propagation may be described as follows. The burnt matter has larger temperature and thermal conduction transports energy from the hot burnt matter to the cold fuel. The temperature of the fuel close to the burnt matter increases, the reaction in this fuel goes faster until another portion of the fuel is burnt and some additional energy is released. The released energy is transported by thermal conduction to the next fuel layer resulting in propagation of the reaction front. Thus, a flame or deflagration is the combustion regime, which is due to heat diffusion – the direct transfer of heat from the burning gas to the fresh fuel, which is still unburned.

Flame velocity and thickness of a flame front may be estimated on the basis of a simple dimensional analysis (Landau and Lifshitz, 1987). If the burning process is characterized by the typical time $\tau_b$, then the only combination of velocity dimension that may be constructed out of the thermal diffusivity $\kappa/\rho_f C_p$ and the reaction time $\tau_b$ is

$$U_f \propto \sqrt{\frac{\kappa}{\rho_f C_p \tau_b}}, \quad (1)$$

where $\kappa$ is the coefficient of thermal conduction and $C_p$ is the specific heat of the fuel at constant pressure and $\rho_f$ is the gas (fuel) density. Obvious conclusion from the estimate Eq. (1) is that the smaller the reaction time and the stronger the thermal conduction, the faster flame propagates. Acting in a similar way, we can obtain expression for the flame thickness

$$L_f \propto \sqrt{\frac{\kappa \tau_b}{\rho_f C_p}}, \quad \text{or being expressed in term of the flame velocity}$$
The equations (1) and (2) are a simple dimensional consequences of the equation of thermal conduction.

If we use the estimate for thermal diffusivity coefficient expressed through the sound speed $c_s$ and the mean free time $\tau_{\text{coll}}$: $\kappa \rho_f C_p \approx c_s^2 \tau_{\text{coll}}$, then we obtain $U_f/c_s \propto \sqrt{\tau_{\text{coll}}/\tau_b}$. Since only a very small fraction of colliding molecules participates in chemical reactions because of the large potential barrier of a reaction (because of a large activation energy), so $\tau_{\text{coll}} \ll \tau_b$. We come to the conclusion that velocity of flame propagation is much smaller than the sound speed: $U_f \ll c_s$.

Typical velocities of the flame range between 5 cm/s and several meters per second. Flame in the hydrogen-oxygen mixture propagates with the velocity about 9 m/s and it is one of the fastest one, while the flame in the mixture 6% CH$_4$ and air is one of the slowest ones with the velocity 5 cm/s. Such slow flames are usually close to extinction limits because of some inevitable losses. With representative values for $\kappa$, $C_p$, and $\rho$ for gas mixtures we find that the typical thickness of combustion zone ranges from $5 \cdot 10^{-2}$ to $5 \cdot 10^{-4}$ cm.

If we consider another type of a flame instead of chemical one, then the energy release may be supplied from other sources. An example of other energy sources is thermonuclear reactions in Supernova flames (Timmes and Woosley, 1992) or the laser radiation absorbed by plasma layers close to the critical surface of a target in inertial confined fusion (Manheimer et al. 1982). For any kind of flames the released energy is transported by thermal conduction and flame propagates relatively slow compared with the sound speed. This is a subsonic regime of reaction propagation.

Flame is not the only possible self-supporting regime of reaction propagation. A reaction can also propagate in a fast supersonic regime of detonation (Landau and Lifshitz, 1987). In the case of a detonation the reaction is induced by a shock wave compressing and heating the fuel. The burning mixture expands and acts like a piston pushing a leading shock and supporting the detonation. From the technical point of view detonation is a very undesirable process that can damage engines. Transitions from the slow regime of flame propagation to a detonation regime are observed quite often in experiments (Shelkin, 1940, 1966; Zeldovich et al., 1985).

Sometimes a third regime of burning is distinguished, which is the regime of spontaneous reaction (Zeldovich, 1980). A spontaneous reaction corresponds to the configuration of a fuel with a non-uniform initial temperature distribution. In this case subsequent (though independent) development of the reaction in the neighboring fuel layers may be interpreted as propagation of a reaction front with the front velocity depending on the initial temperature distribution. Though the regime of spontaneous reaction is much more specific than the regimes of flame and detonation, it may be also interesting from the point of view of flame/detonation ignition.

3. STRUCTURES OF PREMIXED FLAMES

Structure and propagation velocities of gaseous premixed laminar flames depend on transport properties of the fuel gas and chemical-kinetic rate parameters. Questions of interest include the local structure of the flame front, and the most important - velocity of the flame. Structure and dynamics of a flame is described by the hydrodynamic equations of mass, momentum and energy conservation with the account of reaction kinetics and transport processes of thermal conduction, fuel diffusion and viscosity. If for the sake of simplicity we assume a single irreversible reaction, then the governing equations are the following:

$$L_f = \frac{\kappa}{\rho_f C_p U_f}$$ (2)
\[ \frac{\partial}{\partial t} \rho + \frac{\partial}{\partial x_i} (\rho v_i) = 0, \quad (3) \]

\[ \frac{\partial}{\partial t} (\rho v_i) + \frac{\partial}{\partial x_j} (\rho v_j v_i + \delta_{ij} P - \tau_{ij}) = \rho g_i, \quad (4) \]

\[ \rho e + \frac{1}{2} v_i v_i \left( \frac{\partial}{\partial x_i} \rho + \frac{1}{2} \rho v_j v_j + q_i - v_j \tau_{ij} \right) = \rho g_i v_i, \quad (5) \]

\[ \rho \frac{\partial Y}{\partial t} + \frac{\partial}{\partial x_i} \rho v_i Y - \kappa L e_{CP} \frac{\partial Y}{\partial x_i} = -\frac{\rho^a Y^a}{\rho_R^{a+1}} \tau_R \exp \left( -\frac{E}{T} \right), \quad (6) \]

where \( Y \) is the fuel mass fraction, \( e = Q Y + C_v T \) is the internal energy, \( h = Q Y + C_p T \) is the enthalpy, \( C_p \) and \( C_v \) are specific heats per unit mass at constant pressure and volume respectively, their ratio determines the adiabatic exponent \( \gamma = C_p / C_v \), \( g \) is a gravitational field. In the development of the reaction the fuel fraction changes from 1 to 0. We consider a reaction of the order \( n \) with the energy release \( Q \); the Arrhenius law gives the temperature dependence of the reaction rate with the activation energy \( E \) (taken in temperature units) and with constants of time dimension \( \tau_R \) and density dimension \( \rho_R \). Usually the reaction order is of no importance for hydrodynamic properties of a flame with the exception of the problem of flame dynamics in a closed burning chamber, where flames with the first, second and third order reactions behave in a different way. The stress tensor and the energy diffusion vector are given by the formulas

\[ \tau_{ij} = \kappa Pr \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \frac{\partial v_k}{\partial x_k} \delta_{ij} \right), \quad (7) \]

\[ q_i = -\kappa \frac{\partial T}{\partial x_i} - Le \kappa \frac{Q}{C_p} \frac{\partial Y}{\partial x_i}, \quad (8) \]

where \( Pr \) is the Prandtl number characterising the relative strength of viscosity and thermal conduction and \( Le \) is the Lewis number that shows the relative role of fuel diffusion and thermal conduction. Generally, the gas mixture can be treated as a perfect gas with the equation of state

\[ P = \frac{\gamma - 1}{\gamma} C_p \rho T. \quad (9) \]

The set of equations (3)-(9) is typically used in direct numerical simulations of flame dynamics.

The simplest configuration of a flame is a planar stationary flame. The problem is considerably simplified in the case of a planar stationary flame. In the reference frame of the flame front the flow consists of a uniform flow of the fresh fuel mixture entering the flame front with the velocity \( v_z = U_f \), of the region of heating and reaction (which is the flame front itself) and of a uniform flow of the burnt downstream. Then, the structure of the heating and reaction region and the velocity of the planar flame front as a function of the thermal and chemical fuel parameters can be found by solving a stationary version of the equations (3-9) with the boundary conditions in the fuel and in the burnt matter.
\[ T = T_f \text{ for } z = -\infty; \quad T = T_b \text{ for } z = \infty. \]  

(10)

The temperature of the burnt matter depends only on the fuel temperature and the energy release in the reaction and may be expressed through the expansion coefficient as \( T_b = \Theta T_f \).

Equation (2.21) together with the boundary conditions (2.24) constitute an eigenvalue problem, where the flame velocity \( U_f \) is the eigenvalue and the flame internal structure \( T = T(z) \) is the eigenfunction.

The Zeldovich - Frank-Kamenetski theory of planar stationary flames takes into account the fact that typically the activation energy of the reaction is very large \( E/T > E/T_b \gg 1 \). This asymptotic (analytical) theory is in very good agreement with numerical solution of Eqs. (3-9) (Liberman et al., 1994). Characteristic thickness of the reaction zone \( L_R \) where temperature is close to the final value \( (T_b - T)/T_b \ll T_f/E \) is much smaller than the total flame thickness \( L_R \propto L_f T_b/E \ll L_f \). For the flame thickness we obtain

\[
 \frac{\kappa_b T_f^2 (\Theta - 1)^2}{2C_p L_f} = \frac{\rho_f T_f^4}{\tau_R T_b E^2} \exp(-E/T_b). 
\]

(11)

and for the flame velocity

\[
 U_f = \left( \frac{2\kappa_b}{C_p \rho_f \tau_R} \right)^{1/2} \frac{\sqrt{\Theta} T_b}{\Theta - 1} \frac{E}{2T_b} \exp \left( -\frac{E}{2T_b} \right). 
\]

(12)

These expressions are consistent with the predictions of the dimensional analysis Eqs. (1,2).

Figs. 1(a,b) illustrate schematically the flame structures for premixed flame (1a) and diffusion flame (1b), respectively, calculated with a simplified assumption of one-step Arrhenius chemistry based on activation-energy asymptotic for large Zel’dovich numbers.

4. HYDROGEN, CARBON MONOXIDE, HYDROCARBON PREMIXED FLAMES

The structure of flames is determined by competition between radical formation and radical consumption reactions and differs considerably from the structure obtained from one-step high activation energy models. For example, thickness of the reaction zone obtained from one-step high activation analyses is small compared with the flame thickness derived from the maximum temperature gradient. For real kinetics they are of the same order. Furthermore, at least two chemical time scales are necessary to describe the structure of practical laminar premixed flames: one associated with the chain branching of radical reactions and another associated with the three-body recombination reactions. In industrial applications we deal with situations when the flame front is affected by the turbulence already present in the flow or generated by the combustion process.

Abilities to describe all types of data have progressed during the past years; most notably, there has been remarkable progress in determining chemical-kinetic rate parameters. Nevertheless, it needs to be borne in mind that typical uncertainties in values of high-temperature transport properties are on the order of 10% or more and generate uncertainties of about this same order in computed flame structures. The major barrier, however, is the much larger uncertainties in chemical-kinetic parameters, combined with difficulties in computing flame structures with detailed chemistry. Flame-structure calculations with detailed chemistry used to be arduous tasks pursued by only a few devoted experts. Most rate parameters of combustion chemistry used to be deduced from fits to overall measured combustion properties, leading to large uncertainties, often exceeding an order of magnitude, because of
interdependencies of various unknown rates, for example. Presently the rate of the single most important elementary reaction in combustion, the branching step $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$; is known to be better than 5% over the temperature range of interest in combustion. Current direct numerical simulation for turbulent premixed flames is mainly for one-step high-activation energy kinetics for 3D modeling or employs more or less realistic kinetics for 2D simulations.

*Hydrogen–air flames* are special in that no more than about 20 elementary reactions are relevant to their primary chemical kinetics, and the rate parameters for these are known better than those of other flames. There still are uncertainties, such as third-body efficiencies and associated temperature dependences for recombination steps such as $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$. Empirical one-step Arrhenius approximations for hydrogen–air flames required comparatively low overall activation energies, and detailed chemistry descriptions is needed.

Systematically reduced chemistry has been studied in efforts to further clarify hydrogen–air flame structure. Systematic reduction of the chemistry is achieved by introducing appropriate steady-state or partial-equilibrium approximations into detailed chemistry and neglecting terms and reactions of lesser importance to achieve simplified descriptions of the flame structure. This kind of approach has been known since the work of N.N. Semenov.

From the viewpoint of reduced chemistry, hydrogen oxygen flames are relatively simple even with no reduction, since they involve only the eight species $\text{H}_2$, $\text{O}_2$, $\text{H}_2\text{O}$, $\text{H}$, $\text{OH}$, $\text{O}$, $\text{HO}_2$ and $\text{H}_2\text{O}_2$ and possess two element conservation equations. The full-chemistry description is only a six-step description, as judged from the viewpoint of the number of overall steps that are derived by reduced chemistry.

Steady-state approximations for the intermediate $\text{H}_2\text{O}_2$, $\text{HO}_2$, $\text{O}$, $\text{OH}$ and $\text{H}$ results in five, four, three, two and one-step reduced-chemistry descriptions.

In the one-step description, $2\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$ proceeds mainly at the rate of the three-body elementary recombination step. This extent of reduction gives a terrible result, while the two-step description

$$3\text{H}_2 + \text{O}_2 \leftrightarrow 2\text{H}_2\text{O} + 2\text{H} \quad (13)$$

$$2\text{H} \leftrightarrow \text{H}_2 \quad (14)$$

is much better. Here step (13) proceeds mainly at the rate of the aforementioned chain-branching step and step (14) at the rate of the recombination step. Even at this stage, the description is not very accurate, since OH and O do not strongly obey good steady states, but it provides a qualitatively much better description and does contribute significantly to understanding of the flame structure.

The active radical $\text{H}$ is needed for flame propagation: the branching rate

$$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \quad (15)$$

that generates radicals increases with temperature, while the recombination rate

$$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (16)$$

is nearly independent of temperature.

The downstream reaction zone where branching occurs can be very broad and extend over most of the temperature range.

This concept of flamelet structure differs from that of one-step activation-energy asymptotics, which can be made to fit the picture only by having a fairly broad reaction zone, thereby requiring rather low activation energy. This explains why one-step Arrhenius approximations need overall activation energies that vary with conditions.
Carbon monoxide flames share a lot in common with hydrogen flames because they generally need the hydrogen oxygen branched chain to propagate.

The methane–air flame is the simplest hydrocarbon flame. The hydrocarbon chemistry, however, consists of much larger the number of elementary steps that must be considered to address its structure with detailed kinetics and substantially increases the number of chemical species involved. Although the most relevant chemical rate parameters are now fairly well known, the situation certainly is not as satisfactory as that for flames of hydrogen or carbon monoxide. The detailed reaction mechanism in current description of the oxidation of n-heptane includes 2450 elementary reactions among 550 chemical species.

In view of the large number of elementary steps, concepts of reduced chemistry is much more helpful for hydrocarbon flames than for hydrogen flames. For methane–air flames, a four-step reduced-chemistry description has been identified, which includes the fuel-consumption step

\[
\mathrm{CH}_4 + 2\mathrm{H} + \mathrm{H}_2\mathrm{O} \Leftrightarrow \mathrm{CO} + 4\mathrm{H}_2, \quad (17)
\]

in addition to steps (13, 14) and the overall step

\[
\mathrm{CO} + \mathrm{H}_2\mathrm{O} \Leftrightarrow \mathrm{CO}_2 + \mathrm{H}_2, \quad (18)
\]

which is at the rate of the elementary step \( \mathrm{CH}_4 + \mathrm{H} \Leftrightarrow \mathrm{CH}_3 + \mathrm{H}_2 \). The fuel chemistry, proceeding through methyl, formaldehyde and formyle, has the net effect of removing radicals, as indicated by step (18). Consequently radicals tend not to exist where there is an appreciable amount of fuel. An effective overall activation energy can be defined and it does depend on rate parameters of elementary steps, but not in a simple way, contrary to the classical one-step Arrhenius description.

5. POLLUTANT PRODUCTION

During the past years, environmental concerns have prompted extensive consideration of emissions of pollutants from flames, leading to clarifications of finer details of flame structures. Different pollutants force focus on different chemistry, since the chemical kinetics is specific to the pollutant. Addressing emissions of oxides of sulfur, for example, therefore leads to consideration of sulfur chemistry. Much of the recent research has been devoted to the formation of polycyclic aromatic hydrocarbons and of oxides of nitrogen, as well as to emissions of soot. It therefore seems convenient to place the work in two broad classes, namely production of larger molecules through fuel chemistry and production of oxides of nitrogen through nitrogen chemistry.

Pollutants derived from fuel chemistry include both PAH species and soot, one of the contributors to emissions of particulate matter. The chemical kinetics of PAH and soot in flames is very complex and involves very large numbers of elementary chemical steps among large numbers of trace species. In addition to these chemical challenges, soot further involves particle nucleation, growth, coagulation, agglomeration and also oxidation, since the burnup of soot particles once they are formed is a significant process.

Much more research is needed along such lines, the focus being on processes occurring during fuel consumption in fuel-rich flames, an area in need of much further clarification.

Understanding of the problem of production of oxides of nitrogen is in much better shape as a consequence of its greater simplicity and extensive research - the problem is by no means simple, but it is less complicated than the fuel chemistry problem. It becomes necessary to add nitrogen chemistry to the flame chemistry, and this can greatly increase the number of elementary steps. There are various tabulations of rates of the important elementary steps (Miller, Bowman, 1989). One scheme adds 52 elementary steps to include the necessary
nitrogen chemistry (Hewson, Bollig, 1996; Hewson, Williams, 1999). The chemistry in this case can become fairly complicated.

A simplification associated with pollutant production is that the pollutants typically are present in trace concentrations and do not modify the main flame structure. The flame structure can be determined in advance, ignoring the pollutants, and the pollutants can be addressed afterwards. Since pollutant production arises from specific species in the flame, however, reasonable prediction can require relatively detailed knowledge of flame structure. Reduced chemistry can help in sorting out ideas here, as well.

For example, for NO production, the simplest reduced-chemistry step is \(2N + O_2 \leftrightarrow 2NO\) proceeding at the sum of the rates of the elementary steps \(O + N_2 \rightarrow NO + N\), which is followed by \(N + O_2 \rightarrow NO + O\) in the thermal mechanism, \(CH + N_2 \rightarrow HCN + N\); also followed rapidly by \(N + O_2 \rightarrow NO + O\); as well as later conversion of HCN to NO, the prompt mechanism) and steps that follow \(O + N_2 + M \rightarrow N_2O + M\).

The CH comes from the fuel chemistry, primarily from acetylene through methylene, and to obtain reasonable CH concentrations it has been found desirable to take acetylene out of steady state, adding to the fuel chemistry the overall step \(2CO + H_2 \leftrightarrow C_2H_2 + O_2\) the rate of which is largely that of \(2CH_3 + M \rightarrow C_2H_6 + M\).

Peak flame temperature must in general be below about 1800 K for the prompt contribution to begin to be dominant; the thermal contribution is more strongly temperature dependent. The prompt mechanism becomes of concern in designs attempting to reduce NO emissions to very low levels.

6. SELF-ACCELERATION OF FLAMES – FLAME INSTABILITIES – VELOCITY OF PROPAGATING FLAMES

Flames instabilities

It is well known that a flame propagating in a tube rather seldom shows as a planar front, but acquires a curved or even corrugated shape, which is accompanied by considerable increase of the flame velocity. Similarly, a spherical flame spreading out from the ignition point appears not as the outward propagating smooth spherical front but as a multiple-scale resembling a fractal structure. It was well established that the flame is intrinsically unstable against small perturbations bending the flame front. There are two principle mechanisms of the flame instability. The first one is known as the hydrodynamic instability discovered by Darrieus and Landau (LD instability). The LD instability is inherent to all flames in gaseous mixtures since the instability is related to the gas expansion in exothermal reactions. The expansion coefficient is the ratio of the fuel density and the density of the burnt matter and for laboratory flames \(\Theta = \rho_f / \rho_b \approx 6 \div 10\).

Since thickness of a flame front is much smaller than any hydrodynamic length-scales, in the first approximation the flame front can be treated as a surface of zero thickness separating the fresh fuel and the burnt matter and propagating with a constant velocity \(U_f\) with respect to the fuel. In this approximation Darrieus and Landau (Landau, 1944; Darrieus, 1945) found that the flame front is unstable against small perturbations bending the front with the growth rate of perturbations

\[ \sigma = \Gamma U_f k, \]

where, \(k = 2\pi / \lambda\) is the perturbation wavenumber (\(\lambda\) is the wavelength), and numerical factor depends on the expansion coefficient \(\Gamma(\Theta) = \Theta \Theta + 1 \left( \Theta + 1 \right)^{1/(\Theta - 1)}\).
If dissipations (viscosity, thermal conductivity) are taken into account, then the growth rate is limited for a short wavelength (Clavin and Williams, 1982; Pelce and Clavin, 1982; Liberman et al., 1993, 1994). In the linear theory, the growth rate of small perturbations becomes

$$\sigma = \Gamma U_f k \left( 1 - \frac{k \lambda_c}{2\pi} \right),$$  \hspace{1cm} (20)

where $\lambda_c$ is the cut-off wavelength for which the instability is suppressed by thermal conduction. For the case of unit Lewis number and the constant thermal conduction coefficient the cut-off wavelength is given by the formula

$$\lambda_c = \frac{\pi L_f (\Theta - 1)}{\Gamma \sqrt{\Theta + 1 - 1/\Theta} \left( 1 + \Theta \ln \Theta \frac{\Theta + 1 + 2\Gamma}{(\Theta - 1)^2} \right)}. \hspace{1cm} (21)$$

The cut-off wavelength depends only slightly on thermal expansion, and for the flames with $\Theta = 5 – 10$, it takes value $\lambda_c \approx 20 L_f$. The fastest growing perturbations have wavelength $\lambda = 2 \lambda_c \approx 40 L_f$.

In the presence of a gravitational field the LD instability is amplified by the Rayleigh-Taylor (RT) instability for the flames propagating upwards ($g > 0$), and the gravity plays stabilizing role downwards propagating flame ($g < 0$). Taking this into account, new promising possibilities to govern the burning rate open for flames interacting with acoustic waves.

**Velocity of a curved propagating flame**

It was pointed out above that one of the main reasons for a flame to lose its initially planar (smooth) configuration is the flame instability. Because of the instability, small perturbations of a flame front grow and bend the front. Saturation of the perturbations growth is due to nonlinear effects, which leads to formation of stationary curved flames and to a considerable increase of the flame velocity compared to the velocity of a planar flame. Outcome of the LD instability at the nonlinear stage may be wrinkling of the initially planar flame front, which may lead to the stationary cellular structure of the freely propagating flames (Fig.2), or to a smooth curved shape of the flame propagating in tubes (Fig.3). Since the surface area of a wrinkled flame increases with the wrinkling development, the flame consumes more fuel per unit time and propagates faster. Typically, in the case of $Le < 1$ (usually – lean flames) the scale of cellular structure induced by the diffusive instability is controlled by the maximum growth rate of small perturbations. The LD instability favors large-scale structure controlled by the hydrodynamic length-scales of the system, for example, tube diameter.

The shape and velocity of a laminar flame traveling through a combustible gas in many respects depends upon hydrodynamic instability arising at a planar flame front. A planar flame front becomes spontaneously curved due to the LD instability and may, in principle, acquire a steady cellular structure. Curved shapes of flames in tubes have been observed both in experimental studies and in numerical simulations (Liberman et al. 1994, Kadowaki, 1995, Kadowaki, 1995a Denet, Haldenwang, 1995, Bychkov et al., 1996, Bychkov et al., 1997, Bychkov et al., 1997a, Kadowaki, 1999, Travnikov et al., 1999). Typical evolution of the initially planar flame propagating in a tube is illustrated in Fig.3.

While the wrinkling of flame front is well documented experimentally, there have been many controversies in both physical origin and modeling of this phenomenon (Bychkov and Liberman, 2000). Difficulties encountered in trying to obtain a closed description of flame propagation are first of all conditioned by the fact that the process is essentially nonlinear and nonlocal. The gas flows both upstream and downstream are strongly affected by the flame
front structure itself. One of the most important features of non-locality of the flame propagation is the vorticity produced by the curved flame downstream, which highly complicate the downstream flow structure (Fig.4). The main reason underlying the complexity of the problem is the hydrodynamic instability of flames. In view of this, evolution of the flame front cannot be prescribed in advance and should be determined in the course of joint analysis of the flow dynamics outside the flame front and the heat diffusion inside. Nonlinear interaction of different perturbation modes under the smoothing influence of thermal conduction leads to the formation of a steady curved flame front with the curvature radius of the order $20L_f$. This estimate follows from the linear theory of the LD-instability, where it corresponds to the cut-off wavelength $\lambda_c$. Notice, that analysis of the nonlinear development of the LD-instability, in particular, formation of the stationary flame configurations, is highly complicated since it cannot be carried out perturbatively for arbitrary gas expansion. From the mathematical point of view, perturbation analysis is inapplicable because the assumptions of weak nonlinearity and stationarity of the flame contradict each other. Using them simultaneously turns out to be inconsistent except for the case, $\Theta \gg 1$. Only in the case of small gas expansion can the problem be treated both perturbatively and locally, since then the amplitudes of perturbations remain small compared to their wavelengths at all stages of development of the LD-instability and the flow is potential both upstream and downstream in the lowest order in $(\Theta-1) \rightarrow 0$. In this a weakly nonlinear approximation Sivashinsky (Sivashinsky, 1977) has derived the integro-differential equation known as the Michelson-Sivashinsky equation, which describes the evolution of the shape of a flame front. In general case, while the flow is potential upstream where the flow equations can be easily solved, the general solution of the flow equations downstream for the burnt matter cannot be written in a closed form, because the value of the vorticity generated by a curved flame downstream is not known in advance. The presence of vorticity makes the problem essentially nonlocal, since, the value of the pressure field at the flame front is a functional of the velocity field in the bulk.

For the expansion coefficients $\Theta = 6 \div 10$, corresponding to real flames, the nonlinear equations describing curved stationary (Kazakov and Liberman, 2002(a,b)) and nonstationary (Kazakov and Liberman, 2002(c)) flames were obtained recently in a closed analytical form. The velocity amplification of a curved flame is

$$U_w = U_f \left[ 1 + \frac{(\Theta-1)^2}{4\Theta(\Theta+1)} \right], \quad (22)$$

for 2D flames, and about 2 times greater for the 3D flames compared to the flames propagating in 2D channel.

It should be emphasized that the direct numerical simulation of flame propagation for a system of practical interest is a very difficult task even using the most powerful modern computers. For correct calculation of the flame velocity, one has to resolve chemical zone within the flame front, which is about 0.01 mm for typical hydrocarbon flames, while the characteristic length scale of the hydrodynamic flow varies from 10 cm for engines, to several meters for gas-turbine combustors. The problem is even more difficult in the case of turbulent combustion where all the important scales of the turbulent flow need to be resolved. This is why researchers are forced to use a simplified models combined with analytical methods.

**Fractal structure of expanding spherical flames**

Outcome of the LD instability at the nonlinear stage may be wrinkling of the initially planar flame front, which may lead to the stationary cellular structure of the freely propagating flames, or to a curved shape of the flame propagating in tube. If the cell size is large
compared to the cut-off wavelength, then the cellular flame in turn may become unstable against the LD instability on a smaller scale. As a result of this secondary LD instability a fine structure arises on the larger cells. If the largest instability length scale exceeds the cut-off wavelength by many orders of magnitude, then as a result of such cascades of the secondary instabilities consisting of small cells imposed on larger cells, a fractal structure may develop at the flame front (Gostintsev et al. 1988, Filiand, Sivashinsky, 1994, Blinnikov, Sasorov, 1996, Bychkov, Liberman, 1996, Bychkov and Liberman, 2000). This picture is consistent with the fascinating experimental studies by Gostintsev et al. 1988, which indicated that the initially smooth freely expanding spherical flames undergoing wrinkling due to well-developed hydrodynamic instability on the large scales, expand with a noticeable acceleration. It was found that the growth of the average radius with the 3/2 power of time is universal for all the spherically expanding flames

$$R \approx A t^{3/2}$$

The fractal structure of a flame front may be described as cascading humps and cusps: humps and cusps of smaller scales develop on humps of large scales and so on. The general idea of the process may be understood from the Koch curve constructed as a cascade of triangles (Mandelbrot, 1983).

Taking into account similarity of a fractal flame and the Koch curve one can consider a curved stationary flame as one step of the cascade similar to the Koch triangles. In that case one should interpret the curved stationary flame as the generator of a fractal flame structure (Bychkov and Liberman, 1996). In a simple model of an infinitely thin flame front the increase of the flame velocity is equal to the increase of the flame front surface. If a fractal flame has an excess $d$ (a fractal dimension $2 + d$), then the resulting velocity of flame $U_w$ depends on the hydrodynamic length scale, which is the flame radius in the case of spherical flame, $U_w = dR/dt \propto R^d$. This dependence corresponds to self-similar acceleration of a fractal flame

$$R = C_j t^\alpha,$$

with the self-similarity exponent $\alpha = 1/(1 - d)$ which is related to the fractal excess, $d$. The self-similarity exponent, $\alpha = 3/2$, implies the fractal excess $d = 1/3$ and the fractal dimension of the flame 2.33. The corresponding fractal dimension calculated from the flame velocity increase on one step of the cascade of the secondary LD instability, using Eq.(22) gives values 1.2 and 2.3 for 2D and 3D flames respectively, which is consistent with the experiments.

For the flames characterized by moderate turbulence level and high Damköhler number, reaction in premixed flames occurs in a thin sheet known as flamelet. Mandelbrot (1983) suggested that surfaces of constant properties of passive scalars in homogeneous and isotropic turbulent flows possess fractal character. These surfaces should exhibit fractal behavior within a range of scales, which is limited at the low end by the Kolmogorov scale and should be bounded by the large scales of the flow at the high end. The latter can be by order of magnitude, the integral length scale of turbulence, or radius of a spherical flame, for example. It is interesting that in this case the same fractal dimension arises in turbulent flames as for expanding spherical flames. Idea that the LD hydrodynamic instability may act as a generator of the Kolmogorov turbulence seems plausible especially as 3/2 power law is consistent with the scaling law followed from Kolmogorov theory. In contrast to spherical flames, the morphology of the flames propagating in tubes is essentially different, since cascade corrugations merge forming a single cusp whose size is controlled by the tube radius.

There is no final solution to the problem of fractal dimension of a flame front so far; it is still unclear if the fractal flame dimension is a universal parameter. A number of works have
been published (Filiand et al., 1994; Rahibe et al., 1995; Bravo and Garcia-Senz, 1995; Blinnikov and Sasorov, 1996; Kupervasser et al., 1996; Galanti et al., 1998 in attempt to understand fractal nature of laminar and turbulent flames. Results of the recent direct numerical simulation (Liberman, Valiev, et al, 2003) shown in Fig. 6, 7 are seemed to confirm the fractal idea. As is seen from Fig.6, the shape of spherically expanding flame shows amazing similarity of a fractal flame and the Koch triangles. Also, after formation of a fractal structure the regime of the flame propagation approaches the self-similar acceleration regime Eq.(23).

7. DETONATION

Contrary to the deflagration (slow combustion-flame) discussed above, where the propagation through the combustible gas is due to the heat transfer by thermal diffusion, detonation is entirely different regime of propagation of combustion, involving shock waves. The shock wave traveling through the combustible mixture compresses and heats the gas behind the shock front. If the shock wave is sufficiently strong, then the rise in temperature may be sufficient to ignite combustion behind the shock front. Thus, detonation waves are shock waves which are sustained by the energy of the chemical reaction that is initiated by the shock compression and heating. For example, the temperature rise behind the shock wave propagating with velocity $D=2800m/sec$ through $2H_2+O_2$ gas mixture at room temperature is

$$\Delta T = \frac{D^2}{2C_p} \left\{ \frac{1}{\gamma - 1} \left[ \left( \frac{\gamma + 1}{\gamma - 1} \right)^2 - 1 \right] \right\} \approx 1800 K,$$  (25)

which is enough to ignite reaction.

There is no space here to go into details of the detonation theory. The modern detonation models used is the Zel’dovich-von Neumann-Döring model (ZND-model). According to the ZND model a detonation consists of a shock wave traveling at the Chapman-Jouguet (CJ) velocity followed by a reaction zone. The conditions behind the leading shock wave are different from the CJ final conditions, in particular, the pressure and density are much higher than that for CJ. The shock compresses and heats the combustible mixture, which is ignited and begins to react. The overall fuel oxidation consists of a relatively long induction period during which the temperature and pressure of the combustible mixture remains almost constant, followed by a rapid release of chemical energy and temperature increase. The shock wave which is characterized by a very thin front (of order of the molecule mean free path) is followed by the reaction zone – layer moving with the shock, in which combustion is occurring. It is clear that the width of this layer, which is about the speed of the shock wave multiplied on reaction time, $\tau_b$ is much larger than the width of a flame in the same mixture, $L_f \equiv \tau_b U_f$. Thus, the thickness of the detonation wave is about $D/U_f$ times greater than the flame thickness. For example, while the width of the flame in hydrocarbon propagating with velocity $U_f \approx 40cm/s$ is $L_f \approx 10^{-2} cm$, the corresponding thickness of detonation wave is approximately 1 meter. This simple estimate explains that the rise of the temperature in a small spot will ignite a flame but not a detonation.

Gaseous detonation waves have been studied experimentally for many years. Detonation limits, propagation rates, and initiation properties have been examined for many fuel-oxidation mixtures. Theoretical description of detonation shows how hydrodynamic and chemical kinetic processes interact in the detonation waves. The weakest point in the theoretical description and in the existing detonation models is the same as for the flames: this is sub-models for chemical kinetics. Since the induction time plays a crucial role for all models, the lack of reliable chemical kinetic models has been a serious problem.
The first applications of detailed models to compute the detonation induction time using detailed hydrogen-oxygen mechanism have been made in relatively recent time. This became possible due to the simplicity of the hydrogen-oxygen mechanism and the availability of reliable data for the majority reactions involved (see Section 4). For a more complex gas mixtures, for example, hydrocarbon fuels, quantitative analysis is limited by the lack of reliable chemical kinetic models; rates and constants for many reactions are known with a poor accuracy. Difficulties in handling the problem are similar to that the researchers have for the flame modeling when reliable models require coupling 3D hydrodynamic with detailed chemical kinetics.

**Deflagration-to-Detonation transition**

Mechanism of the transition from deflagration to detonation remains one of the most challenging in combustion science. Although significant progress has been achieved in the past years, a comprehensive first-principle understanding of the phenomena is still lacking. It has long been observed that deflagration-to-detonation transition is reluctant to occur in open and obstacle-free systems, but presence of the walls, confined combustion in closed vessels are favorable for the transition.

In a rigorous sense a stationary flame front does not exist without losses, since the fuel always reacts ahead of the flame front though with a very low rate (Zeldovich, 1980; Zeldovich et al., 1985). In reality one may usually neglect the spontaneous reaction in an unbounded fuel due to the large activation energy compared to the initial fuel temperature. Formally this is equivalent to the implicit assumption about some small heat losses in the fresh fuel. The situation is different for flames under confinement. The pre-compression of the fuel ahead of the flame front raises the fuel temperature and density, which may result in a strong decrease of the reaction time ahead of the flame front. Spontaneous development of the reaction ahead of the flame front traveling in a closed tube may trigger detonation at the opposite tube end. For a gaseous combustible in a tube, a flame can experience a transition to detonation only through an unsteady or nonplanar process. Both, expansion of the burned gases and instabilities accelerate the flame and cause two processes that initiate transition to a detonation: emitting pressure waves that propagate in the direction of flame and turbulization. The pressure waves emitted by an asymmetrical curved flame converge to the corner of the tube close to the wall, which the cusp of the curved flame front touches. The pressure waves compress the fresh mixture and rise its temperature. Kinetic energy of the shock is cumulated at the point of convergence. The fuel temperature is maximal at the cumulating points and it is these points, where the detonation starts. The temperature increase can be great enough at the point of convergence to generate local explosions that develop into new propagating deflagration waves moving outward from cumulating points. Eventually, pressures in excess of final detonation pressures develop, and detonation then propagates through the rest of the combustible mixture in the tube.

A criteria of the detonation triggering ahead of the flame front can be expressed as a condition of a self-accelerating reaction ahead of the flame front: the heat release in the reaction must be larger than the adiabatic cooling in the emitted sound wave:

\[
\left| \frac{dT}{dt} \right|_{chem} > \left| \frac{dT}{dt} \right|_{sound}.
\]  

On the basis of Eq. (26) one can calculate position of the flame front when the detonation is triggered as a function of the tube length (Liberman et al., 1998).
**White dwarf burning in Supernova events**

An interesting example of flame dynamics in a strong gravitational field is propagation of thermonuclear flames from the centre of an exploding white dwarf in thermonuclear Supernovae, which are also known as Supernovae of type I. It is a general belief that the thermonuclear Supernovae emerges as a result of explosion of carbon-oxygen white dwarfs accreting mass. Such a white dwarf has burnt already hydrogen and helium, so that the gravitational pressure inside the star is balanced by the pressure of degenerate electrons, which is almost independent of the star temperature. If the white dwarf accretes mass, then the temperature at the white dwarf centre increases and the carbon reaction may be ignited, which happens, when the central temperature of the white dwarf grew above $6.6 \times 10^8$ K. At the moment of the thermal run-away the typical central density of the white dwarf is about $\rho_c = 3 \times 10^9$ g/cm$^3$ and the star mass is close to the Chandrasekhar limit $M_{WD} = 2.8 \times 10^{33}$ g.

Subsequently thermonuclear burning can propagate either in deflagration regime (flame) or in detonation (supersonic) regime. The choice of the burning regime is important in the theory of thermonuclear Supernovae, because it affects the chemical composition of the “ashes” and the total energy of the explosion.

Since the characteristic scale of the problem is of order of $10^3$ km, which is much larger than the thickness of detonation and deflagration fronts, which are of order of $10^{-5} \sim 10^{-3}$ cm and < 0.1 cm, respectively, direct numerical simulation can not answer the question of hydrodynamic regime of white dwarf burning: the grid is too rough to determine the hydrodynamic regime of burning, and the choice of the burning regime becomes inevitably an artifact of a particular simulation.

The flame may be ignited in white dwarfs by a reacting volume of a size of 0.3 m. On the contrary, the reaction has to start on scales comparable to the size of the hot center (about 1 km) of the white dwarf in order to ignite the detonation (Bychkov and Liberman, 1995). As a result flame always starts first in the Supernova explosions. As the flame propagates it forms a bubble of burnt matter separated from the cold fuel by the flame front, which is the surface of the bubble. The density of the burnt matter inside the bubble is smaller than the density of the surrounding fuel, therefore the bubbles are coming to the surface of the star. The bubbles formed from the density of the burnt matter are travelling to the surface faster than they grow when radius of bubbles exceeds $R > 10$ km. The bubble radius is much smaller than the radius of the hot central part of the white dwarf estimated as 100 km. Similar estimates show that the mass of the burnt matter in the bubble of burnt matter is negligible (less than 0.1%) in comparison with the total mass of the hot fuel in the center of the star. Thus the deflagration stage of white dwarf burning is asymmetrical and the hot central part of the white dwarf remains essentially unburned. The unburned fuel at the center of the white dwarf may explode later leading to the detonation regime of burning.

Detonation dynamics in white dwarfs is also strongly affected by hydrodynamic instabilities. Particularly, it has been shown (Kriminski et al., 1998) that thermonuclear detonation is unstable against 1D pulsations of the front for sufficiently large densities of the thermonuclear fuel of the white dwarfs $\rho > 2 \times 10^7$ g/cm$^3$. The instability is similar to the instability of a detonation wave in a chemical combustible with large activation energies of the reaction (Zaidel, 1961; Erpenbeck, 1962; Zaidel and Zeldovich, 1963), which leads to self-quenching of the detonation (He and Lee, 1995; Clavin and He, 1996). Thus, the detonation in white dwarfs cannot propagate at high densities $\rho > 2 \times 10^7$ g/cm$^3$: instead the detonation regime of burning becomes possible only when the white dwarf density has sufficiently decreased due to pre-expansion on the deflagration stage of the star burning.

8. Explosions
Typically explosion is called a process of a violent exothermal reaction where the temperature and pressure are raised very fast compared to the time scales that humans usually consider as ordinary. The explosion can be triggered by an ignition source, or it may develop spontaneously, for example, if exothermal solids are stored in piles that are too large. The term explosion is derived from damaging overpressures that occur.

A well-known example of explosion is undesirable knocking in engine combustion. This abnormal combustion known as knock, which got this nickname from the noise that is transmitted from the colliding of the multiple flame fronts and the increased cylinder pressure that causes the piston, connecting rod and bearings to resonate, has been the limiting factor in internal combustion engine power generation since the discovery of the Otto cycle itself. At present it is generally accepted that SI-engine knock is caused by autoignition in the unburned part of the combustion mixture, the end-gas ahead of the propagating flame, which has not been reached by the flame. Autoignition of the end-gas occurs when the temperature and pressure exceed a critical limit so that comparatively slow reactions, realizing moderate amounts of heat, transform into ignition and fast energy release. Due to the locally rapid energy release, pressure gradients are developed in the combustion chamber, causing pressure oscillations, which results in knocking sounds. It is thus a direct constraint on engine performance. It also constrains engine efficiency, since by effectively limiting the temperature and pressure of the end-gas, it limits the engine compression ratio.

Typically explosion is called ignition of the combustion which is accompanied by a loud noise or clap. Why ignition of a natural gas in the kitchen oven does not produce a noise, but ignition of similar amount of the hydrogen-oxygen mixture looks as an explosion? What do they have in common, what are the differences between ignition of a natural gas and hydrogen?

After the moment of ignition, the burning is a flame front spreading out from the ignition point. The flame front represents a piston, which is moving with acceleration, for example, according to Eq. (23) in case of a spherically expanding flame, into the gas at rest. It is known that if a piston is moved into the gas, then a simple compression wave originates at the piston. In course of time the velocity profile in the compression wave steepens (Fig.9), and initial discontinuity – shock wave is formed at some location ahead of the propagating flame (Fig.10). The time and location where the shock wave will be formed are defined by the envelope of the characteristics intersection which are emitted by the piston, and they can be calculated analytically. Let $R_{\text{shock}}$ is the co-ordinate of the shock formation, $R_{\text{flame}}$ - co-coordinate of the flame front (piston), $D = R_{\text{shock}} - R_{\text{flame}}$. Ratio of the latter values for the methane and hydrogen flames is

$$\frac{(R_{\text{shock}} - R_{\text{flame}})_{\text{CH}_4}}{(R_{\text{shock}} - R_{\text{flame}})_{\text{H}_2\text{O}_2}} \propto \frac{U_f^3(\text{H}_2\text{O}_2)}{U_f^3(\text{CH}_4)} \cong 200 \div 400. \quad (27)$$

In the case of hydrogen ignition, shock wave is formed at about 1 mm ahead of the flame, while flame in methane must travel about 10 cm before the shock will be formed. These simple estimates explain why ignition of a small amount of H$_2$O$_2$ is accompanied by a clap and looks like an explosion. Many people know from their kitchen experience know that the gas ignition at the gas-stove-oven can be accompanied by a clap if gas was ignited after it filled considerable part of oven. The above consideration gives explanation of this phenomena.
CONCLUSIONS

There are many different aspects to the subject. Many important issues of combustion are not addressed in the present lecture, such as ignition, flammability, quenching, chain branching, extinction, thermal runaway, stability of detonation, etc., because of limiting space. The number references that have been cited also does not correspond to a thorough review, but the opposite is in fact true. Only a very small amount of the relevant work has been cited, and the choice of the cited papers was motivated either by the limited space or was not motivated. Many of the particular needs for future research directions have been indicated in the previous sections where the specific topics are discussed. It seems desirable, however, to try to give a more general overview of promising directions for future research. To begin with, there is a strong need in improved numerical models that are 3D hydrodynamical models coupled with detailed chemistry. The unknowns lie almost entirely with the fuel chemistry and complexity in coupling detailed chemistry with 3D flow. This is especially true for various hydrocarbon and alternative fuels that have not been studied thoroughly. A great deal of similar work is needed for better understanding deflagration–to-detonation transition. Another problem of considerable interest and industrial application is the flame – acoustic wave interaction. Development of this kind of information will lead, through improved knowledge, to good methods for governing the combustion process, enhance burning thermodynamic efficiency and to decrease pollutant emission. This work must be both experimental, theoretical and computational. To develop a thorough and correct description of hydrocarbon combustion is a very challenging and important task.

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FIGURE CAPTIONS

Fig. 1  (a) Premixed flame structure on the basis of one-step activation energy asymptotic.
Fig. 1  (b) Structure of a diffusion flame on the basis of one-step activation energy asymptotic.
Fig. 2  Consecutive Schlieren photographs illustrating formation cellular flame structure.
Fig. 3  Numerical simulation of a flame shape evolution in a wide tube.
Fig. 4  Numerical simulation: flow field and vorticity generated by the flame propagating in tube.
Fig. 5  Numerical simulation: flow field and vorticity generated by the flame propagating in engine cylinder.
Fig. 6  Consecutive steps of the Koch curve.
Fig. 7  Numerical simulation showing consecutive configuration of the expanding wrinkled flame.
Fig. 8  Numerical simulation showing average radius of the expanding spherical flame versus time.
Fig. 9  Steepening of the compressive part and flattening of the expansive part in the velocity profile of a simple pressure wave entering gas at rest.
Fig. 10 Envelope of the straight characteristics of the compression wave produced by a uniformly accelerated piston.
MOVIE
Numerical simulation of the flame propagating in tube.
Numerical simulation of combustion in an engine cylinder.
Numerical simulation of spherically expanding flame.

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TEMPERATURE MEASUREMENT FOR MEETING THE EU DIRECTIVE ON WASTE INCINERATION

Elisabet Blom and Dan Loyd
Linköping University, SE-581 83 Linköping, Sweden

ABSTRACT
During the last couple of years, waste incineration has become more sophisticated and more attention is being paid to waste as an energy resource for normal, solid-fuel boilers. The latest version of the EU directive regarding combustion of waste (Directive 2000/76/EU of December 4, 2000) contains still stricter requirements concerning air and water pollution. A fundamental requirement is that the flue gas shall attain a temperature of at least 850 °C for 2 seconds, thereby ensuring that carbonaceous, post-combustion compounds are fully oxidised.

The possibility of using thermocouples for measuring the temperature of the flue gas has been investigated. The project was divided into two parts: one that compared calculated and measured temperatures in a waste-fuel, grate boiler, and one in which measurements were made in a wood-fuel, bubbling-bed boiler. The conclusions of the two parts are presented here.

Temperature measurements were made in a 20 MW bubbling-bed boiler, manufactured by Kværner Co., using type-N and type-K thermocouples. Due to the weather conditions in April 2002, when the measurements were made, the boiler load was reduced to 11.5 MW during the measurements. It was not possible to increase the number of measuring holes in the boiler wall; we had to use the existing ones. The placing of the measuring holes was not optimal, but good enough for showing that thermocouples can be used in this special application.

The thermal boundary layer at the left hand side of the boiler is at least 350 mm wide, which is thicker than expected, since there is relatively good mixing of the gases. The measurements made close to the roof of the boiler showed that the thermal boundary layer was significantly thinner than at the wall; it was suspected that they should be more equal.

The measurements on the left and right hand side of the boiler revealed that the greatest temperature difference between the two sides depended on the load, the fuel, and some other combustion related factors.

Between the thermocouple and the suction pyrometer, differences of up to 70 K were registered, the biggest ones seen during temperature transients. As expected, the time delay of the thermocouples was longer than for the suction pyrometer.

The conclusions of the measurements are:
• Thermocouples can be used to measure the temperature in a boiler, provided that the measurement errors can be compensated for theoretically.
• Thermocouples of type-N perform better in this application than thermocouples of type-K.
BIOMASS AS AN ENERGY SOURCE:
THE CHALLENGES AND THE PATH FORWARD

Elinor Bolyos, David Lawrence1 and Anders Nordin
Energy Technology and Thermal Process Chemistry
Umeå University, Umeå, Sweden
1Chemical Engineering, Linköping University, Linköping, Sweden

ABSTRACT

Modern society is highly dependent upon oil but world oil reserves are limited, corresponding to about 40 years, at the present consumption rate. Additionally, Europe is struggling to develop technologies for reducing CO2 emissions. As a partial solution to these problems, in February 2003, Tony Blair and Göran Persson pledged to double the use of renewable energy sources in the European Union by 2010, so that 12 % of electricity production comes from renewable sources.

Beyond reducing the use of fossil fuels, Sweden has also made it its goal to replace nuclear energy with sustainable use of renewable resources. This goal is supposed to be implemented within an intermediate time period, mainly by the increased use of domestic biomass. Several estimates of present and future biomass fuel supplies have indicated that an expansion from the present 90 TWh/year to a maximum of about 150-210 TWh/year by the year 2025 could be feasible. However, as experience has already shown, switching from fossil fuels to using biomass and waste as fuels introduces some significant challenges that must be overcome. For example, biomass and waste can contain significant amounts of Na and K as well as trace elements such as Hg, P, Cu, Cr, As, Cd, Pb, Zn and Cl. The alkali metals together with P, Zn and Cl have a strong tendency to act as fluxing agents, decreasing the melting point of ashes to the point that, under combustion conditions, they form sticky, corrosive melts that are deposited on boiler surfaces. The deposits greatly reduce heat transfer in the furnace and corrode heat transfer surfaces. In addition, volatile metal chlorides are often formed, resulting in deposition on surfaces, with subsequent Cl-induced corrosion.

Simple measures to diminish these problems by using mixtures of fuels or inexpensive additives, thereby changing the melting and condensation temperatures and the specification of the ash system, have been proposed, but are primarily ad hoc and not guaranteed to work. At this point, solutions to these problems, which will allow biomass to be used sustainably, as desired by the politicians, can only come from increased knowledge of the underlying chemistry involving Na, K and the trace elements under combustion conditions. A survey of the literature quickly shows that there is very little available, especially of sufficient quality to allow models to be developed to allow the extent of fouling and corrosion problems to be identified and studied. The latter, of course, must be the outcome of any work in this area.
Work is currently underway at Umeå and Linköping Universities to determine and model the elementary, gas-phase, chemical reactions that occur when K, Na, Hg, Cd, etc., are released into a combustion environment, as during the burning of biomass. Specially designed reactors have been built and coupled to a molecular-beam, mass spectrometer (MBMS). The latter has seen virtually no use in this field and yet allows the possibility of identifying and quantifying the presence of reactive intermediate species hereto immeasurable. Experience and results from this novel technique will be presented along with the models developed.

**WASTE AND BIOMASS COMBUSTION**

Technologies for combusting waste and biomass have existed for centuries and are today, to a large extent, in use in the Swedish district heating system. It was the oil crisis in the 1970s that initiated the desire to find a domestic source of energy and caused the ideas of implementing waste and biomass combustion to begin to grow. District heating contributes about 44 % [1] of the Swedish heat market and 17 % [2] of the total energy production arises from combustion of biomass. Even so, the dependency upon fossil fuels is still high, which is a problem since world reserves are limited. Additionally, fossil fuels are harmful for the environment and Europe is struggling to develop technologies for reducing CO₂ emissions. As a partial solution to this, in February 2003, Tony Blair and Göran Persson pledged to double the use of renewable energy sources in the European Union by 2010, so that 12% of electricity production comes from renewable sources [3]. Sweden has also made it a goal to replace nuclear power by increasing the usage of domestic biomass, within an intermediate time period.

While the politicians make grand statements about converting from fossil fuels to renewable energy sources, experience in the last 20 years has shown that switching from fossil fuels to using biomass and waste as fuels introduces some significant challenges which must be overcome. Table 1 shows the typical compositions of biomass and waste, and close inspection reveals the problems. First is the high content of volatile matter. As Table 1 shows, a typical biomass contains up to 70% volatile matter. By way of comparison, even a poor, low rank coal does not contain more than 30% volatiles and for a good anthracite, the figure will be as low as a couple of percent. The high volatility may be considered as a positive property (high reactivity) if the combustion technology is adjusted/optimized for these fuels. However, use in existing appliances and plants may result in severe problems. Volatile species are released quickly as a fuel heats up, in the early stages of its combustion, easily creating a fuel-rich cloud, which, if not quickly oxidized, produces significant amounts of heavy tars and soot, especially in small residential appliances. Additionally, if one is trying to use older, fossil fuel furnaces, the large amount of volatiles is likely to lead to combustion being displaced from where it was originally designed to be and, when they represent 70% of the mass of the fuel, it can be said that a significant part of the combustion is occurring in the "wrong" place, affecting the thermal efficiency of the boiler. Traditional technologies for biomass and waste combustion have involved direct oxidation to CO₂ and H₂O, with the challenge being to ensure sufficient local oxygen supply. With the latter in mind, fixed bed systems were replaced by moving or vibrating grid furnaces: the constant motion of the solid particles assisted the heat and mass transfer. In the latter part of the 20th century, the fluidised bed (either bubbling or circulating) was developed; again with idea that the greatly improved heat and mass transfer would increase combustion and heat transfer efficiency. All of these, however, are sensitive to variations in the volatile content of the fuel.
Table 1: The composition of a typical biomass

<table>
<thead>
<tr>
<th>Component</th>
<th>Biomass [%]</th>
<th>Trace elements and heavy metals [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatiles</td>
<td>70</td>
<td>MgO</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>16</td>
<td>P₂O₅</td>
</tr>
<tr>
<td>Ash</td>
<td>0.5</td>
<td>Na₂O</td>
</tr>
<tr>
<td>Moisture</td>
<td>10</td>
<td>K₂O</td>
</tr>
<tr>
<td>Heating value [kJ/kg d.a.s.]</td>
<td>20000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trace elements and heavy metals [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Ash forming elements [%] d.a.s.</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>CaO</td>
</tr>
</tbody>
</table>

More recent technologies aim to combat the latter problem by separating the combustion into two stages: first pyrolyze the biomass in a limited amount of air (just enough, to produce the required heat to do the pyrolysis), producing a gaseous fuel and a solid char (also combustible). The two can subsequently be burned separately in suitably designed furnaces. A modification of this process can be achieved by introducing steam to the pyrolysis stage, gasifying the biomass, producing what is referred to as syngas (a mixture of CO and H₂). This can then be used in a Fischer-Tropsch synthesis to produce synthetic, liquid fuels.

The second problem facing biomass combustion and waste incineration (and perhaps the far more significant one), also appears from studying Table 1: biomass and waste can contain significant amounts of Na and K as well as trace elements such as Hg, P, Cu, Cr, As, Cd, Pb, Zn and Cl. Although fossil fuels, especially coal, can also contain inorganic components, such as potassium, there is a difference in how these components are bound within the fuel. With biomass and wastes the inorganic species are generally very loosely bound, organically or as simple salts, which means that they will vaporize as reactive gas components or affect the composition of the ash to a greater extent than the inorganic species in coal.

Chlorine, together with the alkali metals, can have a strong influence on the corrosion of boiler surfaces in several ways. Typically boiler tubes are made from Ni/Fe/Cr alloys and these are susceptible to accelerated, direct oxidation by Cl₂, HCl, NaCl and KCl. Furthermore, the presence of sulphur compounds can lead to molten alkali sulfate corrosion. Finally, metal chlorides may be deposited on boiler tubes. The nature of the problem is best summarized in a stability diagram for Cr/Fe/Ni-O-Cl. An example is given in Fig. 1 for the Cr/Fe/Ni-O-Cl at 727 °C. Figure 1 shows that at low partial pressures of Cl₂ and O₂, it is the oxides of the metals that will be formed. Oxides are generally very stable, have high melting points and low vapour pressures. As the Cl₂ content increases, however, the metal chlorides are what will be formed and are problematic because, even though they are likely to be solid at furnace surface temperatures, their vapour pressures can be high, leading to vaporization and metal loss. At higher temperatures, the chlorides become molten, causing further problems.
As introduced above, the corrosion associated with Cl-species can result from gaseous or deposited compounds. Beginning with gaseous attacks on boiler surfaces, the most common culprits are HCl and Cl₂. Under oxidizing conditions, if chlorine-species are absent, metal oxides form on the surface of boiler tubes. The oxides hinder further transfer of oxygen into the metal and the rate of oxidation is greatly reduced. Chlorine, however, can diffuse through the oxide layer to reach the metal surface below where it reacts to form chlorides, which diffuse outwards through the oxide layer. As they do so, however, the partial pressure of O₂ rises and, as shown in Fig. 1, the likelihood that they are oxidized increases. The difference, though, is that an oxide layer formed in this manner flakes off easily and does not protect the surface. During the cycle, the Cl₂ is released again and hence it becomes a catalytic cycle:

\[
M(s) + Cl_2 \rightarrow MCl_2(s) \rightarrow MCl_2(g) + O_2 \rightarrow M_3O_4 + Cl_2
\]

Under reducing conditions, the oxide layer on the metal surfaces will likely be non-existent and hence metal chlorides can form directly and subsequently vapourize.

Apart from the direct attack by chlorine-species, solid-phase reactions involving Cl-species in deposits also occur. Lead and zinc chlorides play a major role during waste combustion while potassium and sodium chlorides are the key species during biomass combustion. These species cause significant corrosion, even well below their melting points. The exact mechanisms are not clearly understood, but the two most common theories are (1) that high partial pressures of Cl are formed at the interface between the deposit and the metal, resulting in a mechanism similar to the direct gaseous oxidation described above and (2) that the chlorides form low-temperature melting eutectics which can flux the oxide layer. The high partial pressures of Cl that are formed in theory (1) when the alkali chlorides react with the metal oxide to release Cl₂:

\[
2KCl + Cr_2O_3 + O_2 \rightarrow K_2CrO_4 + Cl_2
\]

The formation of eutectics, as in theory (2), results in molten Cl-species allowing faster reactions, purely because of the liquid phase and also the liquid acts as an electrolyte for electrochemical attack.

Various solutions to these chlorine corrosion problems have been proposed, however, they generally involve mixing fuels or adding inexpensive additives in order to modify the
melting and condensation temperatures and the speciation of the gaseous species. Generally, extensive testing must be completed before these solutions can be judged reliable and, as such, they are not practical in the long run. At this point, solutions to these problems, which will allow biomass to be used sustainably, can only come from increased knowledge of the underlying chemistry involving Na, K and the trace elements under combustion conditions so that detailed chemical models can be built that allow the chemistry of chlorinated species to be predicted. A study of the literature reveals that surprisingly little information about even the basic gas-phase reactions is available.

The gas-phase combustion chemistry of light hydrocarbons is well described by chemical mechanisms from e.g. Bendsten et. al. [10] or GRI [11]. Furthermore, the coupling with chlorine chemistry can be achieved with confidence using the additional reactions of, e.g., references [12-14]. Recent tests conducted by Bolyos et al. [15] indicate that, for conditions typical for biomass combustion, the combination of the Bendsten et. al. [10] mechanism with Roesler et. al. [13] yields the most reliable results.

Beyond the "simple" case of combustion in the presence of chlorine, i.e. combustion including the presence of alkali and heavy metals, there has been relatively little published. There is a small amount of work available presenting chemical mechanisms for combustion temperatures involving sodium, oxygen and chlorine [16-20] with only one [19] giving a detailed chemical mechanism. The rest present some limited experimental measurements of a more global nature, not sufficient for extracting information on the elementary, chemical reactions that are occurring. For potassium, the number of papers is even more limited with virtually no specific reactions. Isa and Lu [21] present some measurements and a global reaction mechanism. However, the latter is fraught with the usual problem of limited applicability. For the heavy metals, the detailed chemistry is mainly limited to mercury [22-24]. It is difficult to find anything for lead, zinc and other elements. The conclusion is that there has been relatively little published on the basic, detailed, gas-phase chemistry of the alkali and heavy metals found commonly in biomass and waste fuels in the presence of chlorine and sulphur.

Work is currently underway at Umeå and Linköping Universities to determine and model the elementary, gas-phase, chemical reactions that occur when K, Na, Hg, Cd, etc. are released into a combustion environment, as during the burning of biomass or waste. A major reason why little work has been done in this area is that it has been very difficult to measure enough chemical species in order to make precise comments about the details of the chemistry that are occurring. Unique in Sweden, The Thermal Process Chemistry group at Umeå University has acquired a molecular-beam, mass spectrometer (MBMS). Problems with traditional sampling techniques include the fact that either sample lines are required to connect an experimental set-up with the analyser and/or chemical components in the sampled gas must be dissolved in a solvent for subsequent analysis. It is never clear for these techniques what is being measured: reactions are likely to continue within the sample line to some degree and also backmixing will occur between the reactor and the analyser. The MBMS samples directly from a reactor and as such avoids the necessity for sampling lines. Additionally, as the sample enters the MBMS it undergoes a sudden temperature and pressure drop. Essentially, gas is drawn continuously through a fine nozzle (0.2 μm in diameter), forming the beginning of a molecular beam. The rapid expansion of the gas effectively quenches any reactions instantaneously, providing an accurate representation of the composition of the gas at the sampling point. Additionally, the non-equilibrium nature of the jet expansion, together with the formation of the molecular beam allows reactive and condensable species to remain in the gas phase at temperatures far below their condensation point, for long periods of time relative to reaction rates. The MBMS is shown schematically in Fig. 2. A sample from a reactor is sucked through three nozzles, creating a molecular beam,
which enters a mass spectrometer (MS), where the gas is bombarded by electrons, ionising it. Because samples can be taken directly from a reaction and frozen rapidly, it is possible also to capture and detect reactive intermediates, which cannot be measured by other techniques. The MS allows species to be identified by comparing a produced spectrum of response as a function of atomic mass (the bombarding electrons fragment the compounds in the sample and the number and molecular weight of each fragment produced gives an indication of the original compound). To quantify the results, i.e. to measure a concentration, a specific molecular weight is used and the response to a given concentration of the original compound is noted. For stable species (e.g. HCl, O₂, CH₄ etc.) a bottle of calibration gas suffices. For intermediate species, a more complicated process must be used. Taking as an example Cl, a key intermediate species in gas-phase chemistry of the alkali chlorides, one must produce it from a reliable source. HCl is one possibility. HCl in the presence of a small amount of H₂ decomposes to a small amount, producing some Cl. If one does this at a known temperature in a reactor long enough to ensure that equilibrium conditions are met, then the concentration of Cl can be calculated using standard equilibrium techniques (in this case the computer programme FACTSage [25] was used). A check also with a calculation including a detailed HCl chemical mechanism, in order to determine the length of time required for the equilibrium to be reached, showed that it was relatively quick (2 s). However, only a very small amount (< 0.001 %) of the HCl is decomposed at temperatures up to 1300 °C. A similar analysis of Cl₂ decomposition reveals that 80% decomposition to Cl can be achieved if equilibrium is reached, however at 1300 °C, 6 minutes is required: far too long to be practical. The final solution reached was to mix HCl and Cl₂ in He, giving concentrations of 1000 ppm, of each. In this case, an equilibrium concentration of 200 ppm Cl is reached in 100 s at 1300 °C.

CONCLUSIONS

- Implementing waste and biomass as fuel in combustion processes to obtain energy and power is a challenge. The challenge being to obtain operational conditions that will sustain the thermal efficiency while limiting corrosion problems. The solution to this challenge starts with increasing the knowledge of the chemistry governing the problematic species, i.e. the alkali metals and trace elements.
- From a political view-point, the potential of waste and biomass is gaining interest, both in response to increasing environmental issues and since it is a domestic fuel.
- So far, no analytical technique has been sufficient for the requirements of measuring inorganic species at elevated temperatures. With the molecular-beam, mass spectrometer combustion species can be measured directly from the hot exhaust gases.
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ENVIRONMENTAL AND ECONOMIC ASPECTS CONCERNING THE REUSE OF EXPLOSIVES

Erik Dahlquist and Emma Nehrenheim
Mälardalen University, SE-721 23 Västerås, Sweden

ABSTRACT
When munitions such as air-bombs and sea-mines are subjected to a disposal process focused on "Resources, Recovery, and Recycling" (R 3), almost all of the explosive is melted and removed from the casing prior to further handling. The casing scraps with the remains of the explosives need, however, to be de-contaminated before the metal can be recovered in a recycling process.

Decontamination, i.e., the cleaning of the emptied casings, is done by means of a burn-out process. In this study, heating the ammunition casings in an open wood fire is compared with heating the casings under controlled conditions in an oven equipped for after-burning of the fumes from the pyrolized explosives. The burned-out casings are sent for re-smelting without further treatment.

An alternative is to cool the casings cryogenically to about -100 °C and crush them before putting the material into the fire or charging it into the oven. The fragmentation method is less risky and, at the same time, the burned-out scrap becomes easier to handle. There may also be a possibility to remove the tars and residual explosive mechanically after cooling, why burning may not be needed.

Our calculations show that the crushing of cooled casings followed by heating in simple wood fires is slightly more economical for a disposal company than using an oven for the burn-out process. However, in a wider perspective, heating in open-air fires costs society twice as much as heating in ovens due to the fact that the resulting air pollution reduces the production of crops and increases corrosion of, e.g., cars. If we can use the cryogenic method without having to heat-treat afterwards this will be the by far most economical way.
EXPLOSION AND FIRE HAZARD ASSESSMENT FOR EXPLOSIVES, AMMUNITION, AND FERTILIZER FACILITIES FOLLOWING EU DIRECTIVE 96/82/EU "SEVESO": CONTRIBUTION FOR GUIDELINES PROPOSAL

Roberto Folchi
Nitrex, Italy

ABSTRACT

The European Directive 96/82/EC, “Seveso II”, requires the quantification of the impact induced in the event of a major accident. However, for explosive materials, no Eurocode, procedures, algorithms, nor specific reference values for damage calculations were specified within the Directive. In order to confirm the validity of “Seveso II Risk Assessments” damage calculations, EU member states can only refer back to their own previously existing legislation on explosives. But calculation methods, scaling laws, and reference values for safety distances vary from one member state to another. Also, the progress that has been made in improving the quality and safety of modern explosives has not necessarily been reflected in all state legislation, some of which is more than 50 years old.

A strong need exists, within Europe, for the adoption of a harmonized approach for assessing the potential damage from major accidents involving explosives. This article illustrates a methodology suitable for use as the basis of achieving a consistent approach within Europe. The procedure presented here is a development of a method first used for undertaking the explosion and fire hazard assessments for mass detonating explosives, which was published in the March/April 2003 issue of the “Journal of Explosives Engineering”. The original method has been further refined, by experience from the consideration of ammunition and oxidising agents, and also extended to include not only the maximum possible impact of an accident but also the maximum probable impact. Formulae for the first approximation calculation of the effects induced in the surroundings by impacting factors due to the occurrence of the accident are proposed. Threshold values for each impacting factors are given with reference to damage severity levels.

A graphical representation of the results from the hazard assessment is achieved by the use of iso-damage areas in which boundaries of the severity damage levels are fixed for each given probability of occurrence of the major accident. A list of bibliographic references is included.
ABSTRACT

Sweden has many wastewater treatment plants that store the process sludge at deposition sites. From the year 2005, there will be restrictions concerning the depositing of any organic waste. This legislation thus calls for the development of new methods or improvement of established techniques for sludge management. This study describes established methods for sludge treatment, degradation of the sludge under different oxygen concentrations, and toxicity of recalcitrant nitro-substituted compounds and their degradation products.

We have examined the sludge produced in a wastewater treatment facility at Cambrex AB, Karlskoga. This facility receives wastewater from a pharmaceutical and an ammunition plant. The sludge contains large amounts of nitro-substituted compounds, which are cytotoxic, mutagenic, and even carcinogenic.

The aim of the study was to use aerobic composting, anaerobic digestion, and constructed wetlands to follow the degradation of nitrosubstituted compounds and changes in toxicity during treatment. The sludge is examined before and after treatment with both chemical analyses and bioassays.

Chemical analysis such as HPLC and GC shows that the concentration of some substances decrease while others increase during the treatment. RDX and HMX were degraded below their detection limits, and all TNT and DNT isomers were reduced during both anaerobic and aerobic treatment. The toxicity tests showed different results depending on which test and species were at hand, and between different treatments. The toxicity tests applied in the study were Microtox, dioxin-like activity, and growth of plants.

In the future, the above-mentioned three biological treatment methods will be evaluated and compared according to degradation and mineralisation potential, and to possible detoxification to find the most suitable method for this particular sludge.
A MOBILE FACILITY FOR DESTRUCTION OF MUNITIONS AND EXPLOSIVES

Nico van Ham
TNO, P. O. Box 45 2280 AA Rijswijk, Netherlands

ABSTRACT
Munitions and explosives that must be destroyed are usually in a poor condition. This is certainly the case with uxo from past wars. Any transportation of these munitions must be avoided. TNO developed a mobile concept for the handling of uxo for the Netherlands MoD. This facility makes use of waterjet cutting and washout to separate the explosives from the metal parts of the ammunition. The explosives are subsequently desensitized by water and additives so that transport and storage will be possible as Class 4.1 materials. Final destruction can be realised in a commercial waste incinerator.
The environmental constraint on all activity in society increases. Conventional munition is not an exception and there is a rising need for new methods to evaluate and to limit the effect that munition has on the environment. This is the subject of a number of research projects at FOI in Sweden. The range of these projects is wide and varies from theoretical studies to the actual measurements at site. This presentation will cover two of these projects.

Life Cycle Assessment (LCA) is a tool to examine the environmental impact of a service or a product over its whole life cycle. In LCA, data is collected from the cradle to the grave for a specific service or product. Using databases and evaluation codes, a picture of the environmental impact is drawn. Hereby, the life cycle part responsible for the most severe environmental impact can be identified, and comparison can be made between different impact sources and other systems. The study also includes the use of a simplified LCA called the MECO method. The MECO is a much faster method but it does not include all the data that a qualitative LCA does. The goals of the project are to get an idea of the impact of the munitions’ life cycle, to see which part/parts have the most severe environmental impact and to see if the qualitative and the simplified LCA differ in result.

The need for new demilitarization methods is accentuated these days, especially the reuse of higher value explosives. Here, the driving force is not only environmental, but also economical. The project aims at the reuse of HMX and RDX. Especially, already available methods are evaluated for different RDX or HMX containing explosives. The examined methods originate from TPL Inc and from Nexplo AB. The project aims to look at how well the selected methods fulfil current and future Swedish needs.

In Sweden, environmental issues take a prominent place even when talking about military materials. Thus the armed forces use FOI to do research for them in the environmental field. This paper describes two projects in the Swedish armed forces environmental research programme.
LCA

LCA is used to evaluate a product’s or service’s impact during its whole life cycle. It is becoming a frequently used method in several industrial areas. The use of LCA when evaluating military materials especially munition is not commonly practise but has been done before (Demex 2000).

This project looks at several aspects of LCA and a possible outcome is for the Swedish Defence Material Administration to use LCA or the simplified MECO method in their acquisition process. At the present time there are no available results from the complete LCA or MECO.

LCA principles

Life cycle assessment (LCA) is the compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle. The life cycle includes mining of raw material, production, use and disposal of a product (i.e. from cradle to grave) (ISO, 1997). The term ‘product’ includes physical products as well as services. LCAs are often used as comparative studies. It is not the products that are compared, but the function of the products.


The analysis is performed in four phases, as described (according to Guinée et al. 2001) and illustrated below. During the process it can be necessary to return to earlier phases to improve them.

- **Definition of goal and scope:** The goal of the study ought to be explained and the intended use of the results, the initiator of the study, the practitioner, the stakeholders and the intended users of the results ought to be specified. A scope definition establishes the main characteristics of an intended LCA study, for example a technical or a geographical study. The function, functional unit alternatives and reference flows ought to be defined in this phase.

- **Inventory analysis:** The product system is defined in the inventory analysis. The definition includes setting the system boundaries, designing the flow diagrams with unit processes, collecting data for each of these processes, performing allocation phases for multifunctional processes and completing the final calculations. The main result is an inventory table listing the quantified inputs and outputs to the environment associated with the functional unit, for example x kg carbon dioxide.

- **Impact assessment:** The results from the inventory analysis is further processed and interpreted in the Life Cycle Impact Assessment (LCIA). This phase includes classification, characterisation as well as the optional phases: normalisation, grouping and weighting. A list of impact categories is defined and it is used to classify the results from the inventory analysis, on a purely qualitative basis. The actual modelling results are calculated in the characterisation phase. The optional normalisation serves to indicate the share of modelled results to a reference, e.g. a worldwide or regional total. The results can be grouped and weighted to include societal preferences of the various impact categories.

- **Interpretation:** The results from the analysis, the choices and assumptions made in the analysis are evaluated, in terms of soundness and robustness. Conclusions are drawn and recommendations are made.
Since LCAs focus on products they are useful for product development, improvement and for comparison when purchasing a product.

It is not possible to quantify everything, so qualitative data and estimations are therefore necessary to create a comprehensive picture even in a quantitative LCA. It is then possible to consider quantitative information in a qualitative LCA, especially when such is easily accessible (Johansson et al., 2001).

**The MECO principle**

The Danish Institute for Product Development and dk-TEKNIK have developed the MECO principle in co-operation with a larger Danish project. The use of the principle is described in “Handbook for Environmental Assessment of Products” (Pommer et al., 2001), which is intended for small and medium-sized companies. The principle divides the assessment into four areas in accordance with the underlying causes of the product’s environmental impacts. These areas, which have given the principle its name, are Materials, Energy, Chemicals and Others (Wenzel et al., 1997).

The information on the studied product/system is first structured in the MECO chart, see Figure 2. The analysis with the chart can be followed by a more detailed LCA, making a gradual evaluation of the product.
All inflows and outflows must be considered for one category at a time with bases on the functional unit and the chosen life cycle phase.

The category ‘Material’ includes all the materials needed to produce, use and maintain the product. Materials that are being reused in the disposal phase are entered in the Disposal box, marked with a minus sign. The use of materials is partly presented as quantity (1a) and partly as resources (1b).

The category ‘Energy’ includes all energy used during the product’s life cycle, including the use of energy during the supply of materials. The use of energy should be indicated as primary energy (2a) and as use of oil resources (2b).

To be able to compare products, the use of material and energy should be calculated as consumption of resources in millipersonreserve (mPR). One personreserve is the resource consumption in proportion to the global reserves of a resource, available for one person, for all future posterity. The use of energy is calculated as use of oil resources.

The category ‘Chemicals’ includes all chemicals in the product’s life cycle. The chemicals are classified as type 1, 2 or 3 according to their environmental hazard level. Type 1 refers to very problematic substances, type 2 to problematic substances and type 3 to less problematic substances. The classification was made by combining EU directives on the marking of chemicals (EU directive 67/548/EEG, European Commission, 1967) and Danish lists, according to:

- **Type 1:** very problematic substances, substances on “Effekliste” and/or “Listen over uønskede stoffer”, ozon-depleting substances.
- **Type 2:** problematic substances: Substances on “Listen over farlige stoffer”, with other R-phrases than fire-and explosion risks. Substances with unknown information
- **Type 3:** less problematic substances: Substances on “Listen over farlige stoffer”, with only fire-and explosion risks. Substances with very little environmental impact.

Environmental impacts that do not fit into the categories described above should be included in the category ‘Other’.

For a detailed description of how to use the method, see Pommer et al. (2001, in Danish) or Hochschorner et al. (2002, in Swedish)

**Application of LCA principles to munition**

For the application of the LCA principles, the 40 mm L/70 PFHE II grenade was chosen. It is a fairly old munition that has been produced in very large quantities. The basis of this choice was that it was old and quite simple in construction, which implied that the amount of available information would be higher than for newer munitions.
There are several goals for this study:

- To identify which aspect of the Life cycle has the largest impact on the environment
- To identify which of the aspects with a large impact that it is possible for the buyer or producer to modify
- To make a comparison between different waste managements and technologies to see the difference in the environmental impact.
- To compare the information you get from a qualitative LCA with the information from a simplified LCA. When would it be wise to use the different methods?
- To make a demonstration case about LCA on military material.

Most of the data were collected in the early stages of the project. The main source of information was the manufacturer Bofors Defence AB. A lot of information on chemical processes was provided by North Carolina State University.

The first simulation showed that there are some specific materials that have a big impact on the environment. One of those was copper and it is important to notice that the impact was significant only if the copper is not recycled. Otherwise chemicals had a big impact, however the validity of that is not certain since there were data gaps in the first simulation.

The final version of the LCA is not finished at the time of writing of this paper so no results can be enclosed here.

**REUSE OF HIGHER VALUE ENERGETIC MATERIALS**

The project “reuse of higher value energetic materials” was initiated by the Swedish armed forces and started in 2002. It is a study of different methods for reclaiming higher value explosives and evaluating them for Swedish needs.

The purpose of reclaiming energetic materials (EM) is foremost an environmental issue. The production of EM has an impact on the environment, though it is important to notice that the reuse of these materials will most likely not have the same large impact as the production of new ones. The method mostly in use in the world today is open burning (OB) and open detonation (OD). These methods are criticized since knowledge of the environmental impact when using these methods is unclear. The use of new methods could clarify the impact on the environment and therefore give a possibility to reduce it.

When reclaiming higher value EM there is also an economical issue involved. When you destroy the EM you destroy an asset. If it were possible to reuse these EM the profit could be substantial, especially if they could be reused for military purposes.

The third and last issue for reusing explosives is that there are fewer and fewer producers of EM in the world. Some production, for example TNT, is located in areas of the world where a safe supply is uncertain. A way of securing a country’s need for EM could be to reuse the EM already in the stockpile. This is doubtful for newer EM but works for bulk EM as TNT.

The part of the Swedish stockpile that is up for destruction today is mostly munitions containing TNT. In the future this will change and a higher amount of munition containing higher value EM will be up for destruction. That will create a need for new “destruction” methods that comply with Swedish legislation and goals for the armed forces.

The major enticement in Sweden for the reuse of EM is environmental impact reduction. Naturally the economical issue is a positive side effect.

This project started with an inventory of accessible methods for reuse of higher value EM and it focused mainly on RDX/HMX-based explosives since these are the EM most common in the Swedish stockpile.
At the beginning of 2003, three methods were identified as having good potential and an evaluation process started. Each process was tested on three explosives. The explosives were chosen based on the binder materials. Those binders were plastic, TNT and wax, which are the most common binder materials in the Swedish stockpile.

The methods derive from Nexplo AB, TPL inc. and are based on three different ways of reclaiming the EM:

- Nexplo AB has a patent for a process that uses organic solvents to dissolve the energetic material. They filter the solution so that only an energetic solution is left and the energetic is then crystallised. The method is mostly used when the binder material is TNT.
- TPL has patented two methods. The first one uses inorganic acids. The acids destroy the binder materials and leaves the EM untouched. The EM only has to be washed to be ready to be used again. This method is mostly used on explosives with plastic binders.
- The second method from TPL uses inorganic salts to dissolve the binder. The binder is then removed from the solution and the EM are collected. This method is mostly used when the binder material is wax.

Currently an evaluation of the methods is underway and the results are not ready to be included in this paper.

The project will continue during 2004 and the next step is to test the methods from this year on newer energetic materials synthesized at FOI.

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ORGANIC COMPOUNDS IN RESIDUES FROM INCINERATION OF MSW AND BIOFUELS

Inger Johansson
Örebro University, SE-701 82 Örebro, Sweden.

ABSTRACT
Organic material in three different incineration residues was examined. The residues were bottom ash from municipal solid waste incineration (MSWI), fly ash from the incineration of biofuels in a heating plant, and a mixture of biofuel and papermill ash. The MSWI bottom ash was examined for water leachable components. Changes of the organic carbon during open-air storage were also followed. Levels of polycyclic aromatic hydrocarbons (PAH) were examined in all three ashes.

The total amount of organic carbon in the MSWI bottom ash decreased during open-air storage. Concentrations of organic carbon in aqueous extracts of the ash were similar, though, resulting in increasing percentage of organic carbon over the course of time. The composition of the water leachable organic carbon changed during the open-air weathering towards an increasing amount of hydrophilic organic acids.

Levels of PAHs in the different ashes varied widely. In the MSWI bottom ash and the heating plant ash the levels were low, but in the biofuel and papermill ash mixture, the PAH levels exceeded the Swedish generic guidelines for PAHs in soil. The distribution of PAHs was similar in all ashes and was dominated by the low molecular weight PAHs naphthalene and phenanthrene.
ANALYSIS OF ORGANIC NITROGEN COMPOUNDS AND THEIR TRANSFORMATION IN BIOLOGICALLY TREATED SLUDGE FROM PHARMACEUTICAL AND EXPLOSIVES INDUSTRIES

Sofie Jönsson, Lillemor Gustavsson and Bert van Bavel
Örebro University, SE-701 82 Örebro, Sweden

ABSTRACT

Many nitroaromatic compounds (NACs) and explosives are of environmental concern because of their toxicity and their tendency to transform to more watersoluble compounds. These compounds are widely spread in the environment due to the large amounts used in industrial and military activities. Complex mixtures can be formed during different degradation and transformation processes in the environment. These mixtures are difficult to analyse. Despite several studies, the transformation processes and reaction products of NACs in soil and water systems are still largely unknown.

In this study, sludge, from a water treatment plant that takes care of wastewater from pharmaceutical and explosives industries, was biologically treated. Transformation and degradation of the explosives and nitroaromatics in the sludge during the different treatments was studied. The sludge was treated under aerobic or anaerobic conditions. LC/MS and GC/MS were used to analyse the explosives and nitroaromatics in the sludge, before and during the treatments. Mass spectrometric detectors can be used for identifying unknown substances by specific fragmentation patterns. LC-MS is used for polar and thermally unstable compounds while GC-MS has the advantage of available spectral libraries for comparison and identification of unknown compounds.

This study showed a decrease in the amount of explosives and nitroaromatics during both the aerobic and anaerobic treatments, except for some pharmaceutical compounds that seem to accumulate in the treated sludge. The degradation of nitroaromatics seems to have been successful for both the aerobic and the anaerobic system.
INVESTIGATION, MAPPING, AND LOCATION OF DUMPED AMMUNITION. A PROJECT OF THE SWEDISH ARMED FORCES

Janne Kjellsson
Swedish Defence Forces, SE-106 87 Stockholm, Sweden

ABSTRACT

Old ammunition and explosives have been dumped in the Baltic Sea, small lakes, and depleted mines up to 1965. So far, the Swedish Armed Forces have mapped 106 different dump sites, most of them in lakes (75) and in the Baltic Sea (25). The locations are spread all over the country. When the Armed Forces started this project, the purpose was to:

• find the exact location for each dumping;
• investigate the risks for the environment and decide what sort of environmental influence is possible in the future;
• assess the likelihood of spontaneous combustion;
• explore the possibilities of salvaging the ammunition, if needed.

A short summary of the results of our investigations and tests is:

• there are no good methods to locate ammunition buried in the bottom sediment of the sea;
• dumped ammunition is not harmful to the environment;
• there is no risk of spontaneous combustion as long as you do not move the ammunition;
• there is no reason, from an environmental point of view, to salvage dumped ammunition.

INTRODUCTION

Old military ammunition and explosives have been dumped in both freshwater, seawater and old mineshafts up to 1965. Up to now we have mapped 106 different locations most of them in small lakes (75), the Baltic Sea and the west coast of Sweden (25). The locations are spread all over the country. When we started the studies on dumped ammunition approximately 10 years ago the fate and effects of the dumping was unknown. Even the exact location was vague sometimes.
The aim of our study was to:

1. find the exact locations for each dumping;
2. investigate the risks for the environment and decide what sort of environmental influence we can get in the future;
3. investigate the possibility of spontaneous combustion;
4. explore the possibilities of salvage the ammunition if needed.

EXACT LOCATION
It is very difficult to find the exact location of the dumped ammunition both in the sea and the lakes in spite of written information, sea charts, maps or other paper where the dumping area is pointed out. This is because of the bottom layer. If the bottom consists of sand, mud, silt and so on, the ammunition will sink down to solid ground and hence are buried in the sediment. In such cases you cannot detect the ammunition with standard methods: sonar, video camera, divers and so on. When the ammunition is buried in the sediment there are no methods to locate the dumping location.

In small lakes it is a little bit easier since we can use ground radar, electromagnetic equipment to detect a target which could be ammunition. After that we must identify the target to be sure it is ammunition and not a cray pot, fish trap or bicycles or anything else made of metal. We have developed a very simple method. We sluice away the sediment around the target with water under high pressure and steer the water tube/hosepipe with a video camera. I can tell you that we have found a lot of metal scrap when we were searching for ammunition. As you can understand this is a time-wasting and sometimes dirty job and up to now we have only investigate 50% of the lakes and 25% of the dumping places at sea.

SPONTANEOUS COMBUSTION
We have tested and examined the possibilities of spontaneous combustion and the result is that there are no risks as long as you do not move the ammunition.

There is a risk that explosives and other organic and inorganic compounds from the ammunition may, if the compounds are water-soluble, pollute and cause serious damage to the environment.

The most harmful substances are trinitrotoluene (TNT) and hexogen (RDX) and/or their degradation products which are toxic to aquatic organisms at low concentrations.

Heavy metals in small quantities, copper, brass and mercury can be found in metal parts of ammunition and fuse bodies but the amounts of these heavy metals are so small that they will probably not affect the environment. Most of a shell consists of iron.

In co-operation with the Defence Research Establishment (FOI) in Umeå and the University of Göteborg, the Armed Forces have tested the risk for environmental contamination. FOI has studied the behaviour of TNT in soil and groundwater under natural conditions and found that TNT will adsorb to the soil. The amount of adsorption will depend on natural conditions at the site. FOI has also analysed sediment and water from different dumping locations and has not found any traces of TNT in the mud. Perhaps this is due to the fact that TNT is enclosed in the shell and the surrounding metal, even after 40-60 years, has not rusted away, meaning that the TNT has no contact with the water or the sediment.

FOI and The University of Uppsala have performed an environmental risk assessment of four selected lakes with dumped ammunition. The results indicate that sediments of many lakes today are heavily contaminated but the contamination cannot be coupled to the dumped ammunition but instead originate from other sources. It is concluded that there is no leakage of explosives from ammunition today and over a short timeframe, dumped ammunition is not an environmental threat.
In the longer term, perspective lakes with a high sedimentation rate will run a lower risk of future environmental impact. In such lakes, the surrounding sediment will retain explosives, probably irreversibly. It can not be excluded however that smaller lakes with very high amount of dumped ammunition and lower sedimentation rate may run a higher risk.

Lake/freshwater and sea/saltwater environments are substantially different. Therefore FOI has mimicked leakage of TNT in a sea environment. Sediment and water from three different sea dumping locations were collected. From the Baltic Sea, one location with aerobic and one location with anaerobic sediment were selected. From the west coast, only one aerobic sediment location was chosen.

The result of this study showed that TNT was rapidly transformed to other metabolites also in a sea environment and was adsorbed firmly to the tested sediment. Lower amounts were bound under anaerobic conditions. The long-term leakage for all sediments was lower than 10% of the total amount bound to the sediment.

The toxicities of water and sediment extract were also investigated on the harpacticoid copepod, Nitocra spinipes. The result showed that neither the water nor the extract of the sediment was acutely toxic to N. Spinipes.

FOI report “Methods for environmental risk assessment of defence-specific chemicals: 1. Explosives” FOI-R-0885-SE, maj 2003, ISSN 1650-1942 presents in brief, work performed in project during the period 1998-2001 as well as the pilot research activities 1994 to 1997.

There has also been field research both in lakes and the sea with A. A. shells cleaved longitudinally to expose the explosive.

The University of Göteborg is studying the effect of experimental dumping of such an A. A. shell in marine sediment –water system in situ.

The pieces of the shell were placed in open boxes with sediment and the boxes were placed at the bottom so the TNT was exposed to the water or the mud. So far the fate and effects have been studied for 2.5 years. The results of this field research are that nothing seems to happen over a short periods, a couple of years. The leaching of TNT is so slow that it is not easily detected. There are the same amounts of TNT left in the shells and the only visible change was a change in colour from yellow to pink.

Sediment samples were also tested for toxicity with bioassays using Daphnia magna, Hyalella azteca and Nitocra spinipes. In some boxes, but not in all, the results suggested that the toxicity was increasing over time but no effects was detected in bioassays with the crustaceans. Therefore, no conclusion on increasing toxicity can be made at present.

The University of Göteborg has also done a laboratory assay of TNT fate and toxicity in seawater and sediment. The objective for this study was to determine its toxicity when added to a sediment water system at a laboratory scale. The result showed that TNT was dissolved passively from an object added to a sediment-water system and had some effect on Nitocra spinipes. This means that the most sensitive organisms in the bottom sediment can be affected negatively at a leaking dumping location. The University of Göteborg will also start a study the effect of TNT on fish.

The result of our research up to now is that dumped ammunition probably is not harmful to the environment and there is only a small risk for environmental contamination. The conclusion is that only small quantities of TNT will be released if TNT is exposed to water in the future. The diffusion will be very slow and the released TNT will be bound very hard to surrounding sediment.

This project will continue for at least 2 more years to elucidate long-term effects of dumped ammunition and to work out a control program so we can follow what happens in the future.

As I have said before most of the ammunition is buried in the bottom sediment.
In a few places however with a bottom of solid ground the ammunition will have an exposed situation and if the lake is shallow it is possible for civilian divers to reach the ammunition which can be very dangerous.

We have therefore tested different methods to salvage this ammunition if needed. Up to now we have salvage ammunition in two small lakes but this is both expensive and dangerous and we will not do it if it is not necessary. Our plan is to do nothing if the ammunition is not harmful for civilians.

To document the information from tests and research we keep a register of every location of dumped ammunition.

**SUMMARY**

There are no good methods to locate ammunition buried in the bottom sediment in the sea.

Dumped ammunition is probably not harmful to the environment.

We will check the long-term effect with a control program every 5 to 10 years.

There is no reason from an environmental point of view to salvage dumped ammunition.
NEW EDUCATIONAL PACKAGE FOR FLAMMABLE MATERIALS

Stefan Lamnevik
Stefan Lamnevik AB, Ersta, SE-640 51 Stjärnhov, Sweden

ABSTRACT
To avoid accidents it is important to understand the properties of handled materials and also to understand the basic phenomena involved in their normal reactions. It is not always safe to rely only on written instructions and rules. Sooner or later you will meet situations where there are no written rules – you may then act according to instinct or knowledge. Here we believe that knowledge is the prime basis.

At FOI, the Swedish Defence Research Agency, there was an early agreement that safety was promoted by knowledge and that all personnel should have a good basic education on explosives and explosives effects before they were allowed to work with explosives. A course was created which has been successively improved and extended, and has now been run for more than 30 years by FOI. Employees from the Scandinavian explosives manufacturers and from governmental institutions also attend the course today. This education is available on CD-ROM.

People working with research and manufacture of explosives also use chemicals. Many chemicals are combustible and highly reactive and may cause fire and explosion. Therefore a basic course on fire and flammable materials should be the next logical step to promote safety, not only for the explosives industry but also for the chemical industry.

PERSPECTIVE FOR THE NEW COURSE
Companies are not so likely to send personnel to courses any more; down-sizing has made them short of people. They want the working teams to be available at the site, not being away on courses.

A realistic possibility is to make the education accessible on demand on the sites and at home through Internet.

Education involves teachers. The role of the teacher is twofold: to help the students (answer questions) and to make sure that they have understood (examination). It is not necessary that the teacher be present in the same room as the student, but it is important that he or she can be reached within a reasonable time, say within 24 hours.

People reading this course will have different backgrounds and experiences and will be of different ages. Therefore it is important to start from a very basic level and include facts on, e.g., units. Also, handling the computers should be easy.
To maximize learning efficiency a combination of text, sound and exercises should be available. This means that multi-media computers would have to be used.

The course should focus primarily on science rather than on regulations. Of course, laws and regulations are necessary to know, but it is better to start with science and follow up with regulations. Doing it that way we will understand more and therefore be motivated to follow the regulations.

THE PEDAGOGICAL IDEA
To describe Flammable Materials we will have to specify what happens in a flame, show how to recognize the various substances, to define what energy is, and show how heat is measured, to show what combustion products are formed, and finally to deduce what the hazards can be from all these facts.

We have seen from the course on explosives that chemistry provides an easy way to understanding, provided it is limited to and focused on the actual problem. Here we introduce only a few of the 92 elements found in nature: C, H, N, O, S, Cl, and some metals. We show how compounds are built from the elements, what empirical formulas mean, and which stable combustion products must be formed from a given substance. For heat of combustion we examine the empirical formula and can then estimate an approximate value.

Combustion is defined as a reaction between gases: oxygen from the air and a combustible gas, combustible vapour or a combustible pyrolysis gas. The conditions for combustion are described, and so are ignition energies and ignition sources.

The hazards described are heat and heat radiation effects and toxic effects of the combustion products.

Prevention and fire fighting are the last elements in the course and are described in the terms learned in the first parts.

PART I: PHENOMENA
This part of the course deals with basic chemistry and physics and has 5 chapters:

- Fire – a chemical reaction
- Ignition
- Energy and power
- Combustion products
- Hazards associated with flammable substances

After each chapter there is a quick test (20 questions with 4-5 answer options) to check the present knowledge. It may be repeated as many times as wanted. To go on it is recommended that more than 17 questions should have been answered correctly.

There are also two questions for each chapter these must be answered in writing. This is done via the built-in mail system. These two questions must be answered correctly for each chapter to get an examination.

In this part of the course there are six “lab exercises”. Here the student can do exercises on chemical formulas and energy units and perform experiments to determine explosion limits and ignition energies, flash points and heats of combustion.

PART 2: FLAMMABLE SUBSTANCES
This part of the course describes flammable substances sorted according to the transport regulations and has the following 5 chapters:
Flammable gases
Flammable liquids
Flammable solids
Substances liable to spontaneous combustion
Substances which give off flammable gases on contact with water

The chapters are ended with quick tests and written exercises and some include “lab exercises” as in Part 1.

Three “lab exercises” are included. They deal with combustion data for flammable gases and metal powders and exercises on chemical formulas.

PART 3: FIRE PROTECTION

In the last part of the course there are the following 5 chapters:

Fire indoors as a scenario
Storage and transportation
Fire fighting
Prevention of fires
Detectors

The first chapter is more or less a summing up of what has been taught in the first two parts of the course, and is focused on a person inside a room that is burning. The impact of heat, concentration of toxic combustion products, and low oxygen concentration on man is described. We added this chapter because we realised that ordinary people do not have the insight into the dangers of trying to enter a room that is on fire, unprotected, to rescue other people or to fetch their belongings.

The chapters are ended with quick tests and written exercises and some include “lab exercises” as in part 1.

“Lab exercises” in this part are calculations of fire load index, total combustion energy divided by total cooling area of the room (floor + walls + ceiling).

TEST COURSES

When chapters 1 and 2 of the course were produced these parts were evaluated by a group of people from the Swedish explosives and chemical industry. They liked the course and found it easy to use and understand. A few had trouble in getting access to the server used by the course through their company firewalls and had to use computers at home.

A reference group with members from the trade unions, the Inspectorate of explosives, the explosives industry and chemical industry monitored the production of the course. They considered the members of the test course to be too well educated (some were engineers) and decided that another test course should be run for “ordinary people” when all chapters were ready.

The full course was tested on a small group of “ordinary people”, some were unemployed. They all finished the course and got their examination. They used more time for it than the first test course, but not more than the nominal recommended time of 150 hours. They all liked the course and were active in communication with the teacher. The need for a teacher was obvious.
COURSE STATUS TODAY

The course has been approved by the reference group and was ready for production in June 2002. The first full course for production people was run in late 2002 with graduation in March 2003. Excellent results were recorded.

The course is in Swedish. Translation to other languages can be made. For information, contact Prevent, P. O. Box 20133, S-104 60 Stockholm, Sweden. Email address: info@prevent.se.
SOIL REMEDIATION: AN OVERVIEW OF EXISTING TECHNOLOGIES

Per-Anders Bergman
Sydkraft SAKAB AB, SE-692 85 Kumla, Sweden

ABSTRACT
In Sweden, excavation and landfilling are, at present, the most prevailing ways of handling contaminated soil. This presentation will provide examples of different remediation methods that result in the destruction of contaminants, or when it comes to metals, ways to greatly minimise the volume of the contaminated soil. All the examples of the methods given here have the following in common: all have been commercialised in Sweden, and all technologies result in soil clean enough for re-use. The presentation clearly demonstrates the broad spectrum of concepts available for treating a variety of contaminants in soil in an environmentally sustainable way.

The presented examples have been selected based on the steady and high frequency of objects polluted with PAH-s, chlorinated solvents, nitroaromatic compounds, and metals. The following treatment methods are described in the presentation:

• for PAH-s – biological field treatment, bio-reactor treatment, continuous wet chemical treatment, thermal destruction.
• for chlorinated solvents – cyclical biological treatment, evaporation and capturing (in situ), thermal destruction.
• for nitroaromatic compounds – cyclical biological treatment, physico-chemical destruction.
• for metals – wet chemical treatment performed in batches or by continuous-flow technology.
Rediscovered documents reveal problems in the Swedish match industry due to contaminated red phosphorus in the 1920s. Over the years, more than 150 match factories were established in Sweden. In the 1860s, the production of safety matches requiring red phosphorus in the friction composition began to soar. The cheaper phosphorus matches with white phosphorus in the head composition were also produced until the white phosphorus ban phased them out in the 1910s. In factory buildings where phosphorus matches were produced, fire accidents often occurred.

During the first world war, Sweden was blockaded by the Allies England and France, and could at the end of the war only import raw materials following the Swedish “Modus Vivendi agreement”. After the war, chemicals that could be imported were of poor quality. As to red phosphorus, the match industry had to learn how it should be purified.

In the spring of 1922, the problems caused by impure red phosphorus escalated, and whole consignments of red phosphorus batches had to be returned to the producer in Germany.

On the 30th of May 1922, Växjö Match factory burned down. To protect the small town from a devastating fire, over 1200 available personnel were put to work at night in order to fight the fire. The police investigation the next day could not conclude any reason for the outbreak of the fire. The day after, boxes with red phosphorus that had been moved to a safe place far away from the fire, ignited spontaneously.

On the 16th of June 1922, a head office memorandum was sent to the Swedish match factories urging them to hermatically solder those metal boxes that contained red phosphorus of poor quality and store them separately.

On the 24th of July 1922, one match factory reported on a test delivery of 500 kg of red phosphorus that it was contaminated with white phosphorus and therefore unlawful to use.

HOW I BECAME INVOLVED

In the 1960s, an elderly man related to me how match waste was handled in the 19th century. His stories awoke in me as I in the spring of 1998 had a cancer tumour removed.

After the operation I was sitting with new friends in the Växjö hospital, looking out over the surroundings. We talked about the town, the people walking around the Växjö Lake,
children playing in the park of Strandbjörket... and I remembered the stories I was told in the 1960s. Those children were playing on top of waste that was placed there in the 19th century – three old rubbish heaps, and between them the dredgings from the Växjö lake.

After being discharged from the hospital, I started to investigate how waste from the match factory was disposed of in the 19th century, and found that burying in swamps was the preferred method. According to the old man, a big empty barrel without lids was pressed down a bit in the wet ground. Waste was then poured through the barrel, which was used as a tube, and sank into the ground. Finally, some sand was shuffled after the waste.

Why was the old man involved in a notable transport in the early 1920s? Secrecy was ordered by a person of high rank unknown to him. Tins should have been transported from Växjö to a location near Kosta, where they were buried in the wetness close to a mere. “Where the person of high rank” clearly marked out the place on a map; why?

**MATCH FACTORIES PRODUCING PHOSPHORUS MATCHES**

In the 1830s bookseller C. G. Södergren (1807-1886) in Växjö became friends with one of the students at Wexiö high school, Johan Edvard Lundström (1815-1888) from Jönköping – later known as “the father of the Swedish match industry”. The friendship established between them is evidenced by numerous saved letters, exchanged between the two families. (VSB SA)

In 1843, the production of phosphorus matches are mentioned for the first time, in a report by the Swedish National Board of Trade. The year after, Professor G. E. Pasch in Stockholm patented his safety match in which phosphorus in the unpoisonous red allotropic modification was used for the striking surface on the match-box.

In 1845, J. E. Lundström started his match factory in Jönköping. The phosphorus manufacturer A. Albright in Birmingham patented 1851 a process for the production of red phosphorus. Being the supplier of white phosphorus to the match factory in Jönköping, he offered it the new product. At the world trade fair in Paris in 1855, the match factory in Jönköping then introduced, what years later was to become the famous, Swedish safety match.
In the 19th century, the popular and cheaper phosphorus matches were the main product of the Swedish match factories. But the demand for safety matches grew steadily, not least due to the banning of phosphorus matches in country after country. At the end of the century, the Swedish safety match had taken the lion’s share of the market.

Over the years, more than 150 match factories were established in Sweden (Appendix 1). Many of the Swedish counties had match factories in what today are town centres.

In the 1860’s, phosphorus necrosis – the phossy jaw illness – among match factory workers escalated. The authorities began to tackle the problems connected with industrial hygiene as well as those connected with the environment outside match factories.

On the 18 February 1870 came the Swedish Royal Decree for match production and for other ignition compositions containing white phosphorus (VLA. JoV. FVIII). The decree stated that:

- Phosphorus was only to be handled in factories that were built for such production.
- Phosphorus should be stored separately under a safety lid, fire safe and frost-free.
- The production manager should have chemical knowledge, verified by a higher institution.
- The factory should be situated on a free and dry place. The different manufacturing processes should be performed in separated, ventilated rooms with ventilation hood over the work places.
- The working rooms should have non-inflammable materials on surfaces, a ceiling height of 10 feet and a floor space of minimum 30 square feet per worker.
- The working room and working places should be cleaned every day.
- The working room surfaces should be washed every two weeks.
- The workers should wear working clothes that were cleaned every day.
- The working clothes should be changed and kept in separate rooms when not used.
- The workers should have access to clean water and washrooms.
- The workers exposure to phosphorus should be documented. Work with phosphorus was maximised to 6 months intervals, separated by minimum 2 months of other work.
- Health control by a factory physician was compulsory and should be made every 3 months.
- All waste should be burned immediately, water used for washing and cleaning should be poured into a separate, deep well.
- The production was only allowed after approved inspection.
- A Magistrate of a city, a City Administration or a County Police Commissioner should do the inspection and completely document observations made.
- A substantial fine was coded for trespassing.
“THE MATADORS”

In 19th century, three men’s work and fighting spirit was popular amongst Växjö people, who called them “The Matadors”. Among other things they saw to it that factories were founded.

Bror Fredrik Ekeroth (1817-1883) was a pharmacist, the first bank director of Skånes Enskilda Bank in Växjö and, through his son, owner of the newspaper “Smålandsposten”. Ekeroth was also a member of the County Administration. He promoted the ideas of a hospital and of schools, that open sewers and the Växjö lake should be cleansed.

Carl Schander (1828-1898) was a trader, owner of the Wexiö Match Factory, the Wexiö Engineering Plant, a cigar factory and the estates Gårdsby, Ringsberg and Westergård. He was also a protector of the world famous soprano Christina Nilsson. Thanks to his engagement, waste handling and water treatment problems were approached.

Carl Gustaf Södergren (1807-1886) was a bookseller and a printer. His historical and technical knowledge, not to mention his net of contacts and acquaintances, made him always the one to be asked. He investigated and cleared up several of Växjö’s historical ownership.

North the Göl
Schander’s Estate
Ringsberg

Dg, Dh, Di and Dk formed the first WTF round.

Ödman is
Schander’s Estate
Westergård.

The western suburbs of Växjö in 1867.
After April in 1868, no rain fell in the southeast of Sweden. By August, people were starving, and in October the first death caused by starvation was registered. Wexiö Match Factory (WTF) was established this “year of famine” in the western suburbs of Växjö, near the Växjö pond. The following year, 1869, emigration from Sweden began to escalate.

On the 28th of November 1868, six months after the permission to build the match factory was obtained from the Wexiö Magistrate, the first match consignment left WTF. (VSB SA)

On the 17th of July 1870 was WTF inspected, following the 1870th Swedish Royal Decree. In the inspector’s handnote is written: “The workers who had to work in the presence of the phosphorus fumes covered their mouths with a box filled with sponge, which was moistened with turpentine.” An early use of gas masks! Turpentine dissolves white phosphorus. To handle the phosphorus gases the first expansion of the WTF factory now takes place, and for ventilation an electrical ventilation system was installed instead of the in those days only known draught chimney that was fired from a separate fireplace.

In the 1870s, WTF was the pride of Växjö. Visitors coming to Växjö on the western main road entered the town centre on a linden avenue. On its northern side the match factory’s symmetrical buildings could be seen with its architectonically remarkable and representative form.
In March 1875, the county governor confirmed Växjö’s fire rules. Indoor storage of combustible material was now limited to the daily need. All other storage should be in a vault cellar or in a stone-built house without fireplace. Traders were allowed to have 2'000 foot-pounds (850 kg) in a building on the same site. Outdoors, and at least 10 feet from such a building, the allowed quantity was unlimited, provided the material was buried and covered with 2 feet of earth or sand.

In February 1875, 46 women died in a fire accident in the Tidaholm match factory. It was at once decided that all Swedish and Norwegian match factories must be inspected regularly (the two countries constituted a union). The former founder of the match factory of Jönköping, J. E. Lundström, got the job as the union’s first match factory inspector. During the following two years, all match factories on the Scandinavian peninsula were rigorously inspected.

In 1877, Lundström’s report over all the 41 Swedish match factories that were in production were announced in the Swedish cabinet meeting.

Johan Edvard Lundström

CALEB WARREN & CO/ SMC, London

In 1887, Schander sold WTF for £ 40 000 to the Caleb Warren & Co in London, Warren acted as a representative for the real owner, the Swedish Match Company Ltd (SMC) in London. Schander remained as manager until 1891.

Four years later, a fire started in a drying box for splint. The box and the ceiling in the splint hall were destroyed. A possible cause for the fire was that a phosphorus match had found its way into the fresh-cut splint that was to be dried in the drying-box.
From the 1st of July 1901, the Swedish phosphorus ban came in force: after that date it was prohibited to sell in Sweden matches containing white phosphorus in the ignition composition. Production for export was allowed until 1920 (but was discontinued earlier).

Phosphorus matches and a phosphorus match label from WTF

In 1913, the production of phosphorus matches ceased at WTF (SmP 1918). The reason was that the U.S.A. had – as did Russia – chosen the method of taxing these matches out of existence.

Model of WTF in 1901, built according to the author’s reconstruction. (SM)

IVAR KREUGER – FROM FSTF to STAB

In the beginning of the 20th century, the Swedish match factories were arranged in two separate groups of companies. The Jönköping & Vulcan, or JV group, was established in 1903, and consisted of eight factories located at Anneberg, Jönköping, Tidaholm, Uddevalla and Westervik. Ten years later, Ivar Kreuger counter the JV group by establishing the United
Swedish Match Factories, FSTF. This group united factories in Gothenburg, Grantorpet, Kalmar, Lidköping, Malmö, Mönsterås, Nybro, Vetlanda and Växjö.

In 1914, Kreuger presented a modernisation program for FSTF. With an investment of SEK 1 300 000, the yearly earnings expected to be SEK 500 000, i.e., pay back in 2.5 years. (VLA JoV)

In 1915, there was a tough negotiation with England about the Swedish need of access to the sea in order to carry on the shipping trade. It lead to the Swedish War Commerce Laws. A temporary agreement with England in May 1916 opened for import from the U.S.A. In July 1916 the allied England and France annulled the London declaration (right of passage) of 1909, and the Paris declaration of 1856. The war led to that the Swedish folk economic administration was nominated in September 1916, and food and raw material became rationed. (RA UD1902)

As it had proven impossible to obtain new supplies of some of the chemicals used in the striking surface on the matchboxes, the decision was taken to limit the striking surface to one side of the box. Announcement in December 1916 by JV TFAB/AB FSTF.

In February 1917, J.Hellner and M.Wallenberg submitted a Swedish trade proposal, which England accepted. But the Swedish government Hammarsskjöld couldn’t balance the left-wing forces and fell on the costs for the Swedish neutralitet gard. The next government Swartz-Lindman fell in the general election in September and as U.S.A unveiled the transmission by the Swedish foreign ministry of German-coded telegrams – the Luxburg affair –, all communication with the Allies was stopped. The new Swedish government – Eden-Hellner-Branting was pressed to start negotiation with the Allies about the most necessary goods to be imported. The negotiations were balanced to avoid an open break with Germany who offered to supply Sweden over German harbours. (RA UD1902)

The JV group chose to divide their import between the two combatants. The Allies punished them for this by refusing to export the required raw materials to them. At the end of 1917, JV had no paraffin or phosphorus left. Officially, FSTF kept their purchase on the Allies’ side. The blockade during the war made it necessary to rationalise the purchase of raw materials. Being under the samwards, an international match trust was established by the Swedish Match Co(STAB). STAB’s profit was reinvested in raw materials, energy, transport and sale.

THE SWEDISH “MODUS VIVENDI” AGREEMENT IN 1918

In 1918, Sweden agreed to transfer Swedish ships to the Allies in accordance with the Swedish Modus Vivendi agreement. (RA UD1902)

The first agreement ratified in March 1918 (“the small negotiation”). Its main parts were secret;
100 000 Swedish ship tonnage were transferred to the Allies for three months. Sweden was allowed to import 75 000 tons of goods. The announcement caused a threat from Germany.

The second agreement was made in May ("the big negotiation"), and was in the main parts strictly secret. A tonnage of another 300 000 was now additionally transferred to the Allies for 12 month. A credit and export privilege was given to the Allies. Import of 1 million tons of goods were strictly regulated and handled by special offices in London and Washington.

Of the transferred ships, 4 % were sunk by mines and German submarines.

During the war, bones were again being used as raw material for phosphorus production for the match industry. In April 1918, the FSTF purchase department announces that 60 tons of phosphorus is enough for 8.5 months of production.

FSTF issued a secret "Circular15" about the lack of chemicals. Secret "Circular 16" of April 27, 1918, called for a three-day working week, added a fringe benefit of 10 %. Two next days of the week are paid with 60 % of an average by the day wages. (VLA JoV FIV)

In order to free the corresponding amount of bones, FSTF began trials with phosphorus made from raw phosphate. (VLA JoV EI)

In August, FSTF announced by secret "Circular 17" that raw materials have been secured with the effect that the working week can be extended to four days. Friday and Saturday are now paid with 60 % of the average wages. (VLA JoV FIV)

The match factories provide their workers with daily food rations. But this autumn of 1918 there is a great shortage of food in Sweden. In addition, half a million people caught the Spanish flu and over 18 thousand people died.

FSTF’s “Circular 51” in September effects that the quality problems of the imported as well as the Swedish amorphous phosphorus are thoroughly analysed. (VLA JoV EVII)

Ivar Kreuger himself puts forward the idea of using apatite for phosphorus production, and in October he asks the Trollhättan phosphorus factory to find out whether this can be possible.

With the issuing of “Circular 66”, the Swedish match industry begins to rationalise and unify the different factory receipts of ignition and friction compositions. (VLA JoV EVII)

**AFTER THE WAR**

The problems during the First World War led to a modern economy with monthly balance of the books. The different goods and quantities are figured out according to what is taken out and given into the stores. Twice every year, on the 30th of June and 30th of November, the whole stock has to be weighed and audited. According to these monthly inventory lists there is multiple index that gives a good picture of the raw material assets and the consumption. (VLA JoV)

![The FSTF inventory list of 19 April 1919.](image_url)
But better quality of amorphous phosphorus was still the most urgent thing.

Manager Modig at Fredriksdal’s match factory offers in 1919 an advise in FSTF “Circular 102” (VLA JoV EVII):

Due to the inferior quality of the phosphorus we have to work with, we have for a long time been forced to wash the phosphorus in two waters before using. We have observed that from 10 kg of phosphorus, we obtained 2–3 % phosphoric acid in the first 15 litres of water. The second 15-liter portion of water contains a negligible amount of phosphoric acid, but the washing should be carried out. Comparison between the ability of washed/unwashed phosphorus to absorb water:

Place the phosphorus over water, under a glass bell, for some days. The washed sample does not absorb any moisture, but the unwashed one absorbs up to 27 % of water.

After the test, the washed phosphorus was in powder form as earlier, while the unwashed sample had degenerated into a paste form, which after a time became liquid delinquents.

FSTF’s “Circular 105” of October 1919 gives instruction for joint formulas for the brown safety mixture and for the striking-surface mixture. Before the new formula for blends are introduced into the production, every factory had to make their own test batches of safety and striking-surface compositions. This work resulted in adjustments, and with “Circular 114” comes more strict analysis methods; all tests should be made in running number, and all possible information should be given as size, deliverer, purchase place, etc. (VLA FSTF)

The correspondence between the factories shows a secondary development of the compositions and new developed techniques for applying the mixtures on sticks and boxes.

**VISIBLE PROBLEMS WITH RED PHOSPHORUS**

In 1920 a fire broke out at WTF. It started in a wooden drum situated between the steam engine room and the production room for miniature matches. (VKA BS)

The phosphorus quality, led in March 1921 to FSTF-Purchase “Circular 16 and 19”. Urgent is asked for further investigations of the batches of phosphorus;

1. How large is your stock of German red phosphorus?
2. Do you have in stock any of the red phosphorus from Trollhättan or from England?
3. Do you think that any quantity, according to your own opinion, could not be used? What else in this case do you have to communicate? (FOAK WTF)

**WTF BURNS DOWN ON MAY 30, 1922**

(VLA, VKA, FOAK, Smp, NVB)

At WTF this Tuesday, the daily work finished at 5 PM, and Sven Jakobsson, the night guard, started his rounds. Every half hour he walks a 12 minutes round. He passes first through the 20 m wide splint hall with its splint lathe and four splint-polishing drums (three bigger and one smaller, named roller) and also eight splint dryers (for drying splint impregnated with phosphate for after-glow prevention).

Cam radiators heated the drying boxes. The heating tubes were installed in the floor. Before the heat came onto the splint, it was mixed with cold air to become dry. The westernmost drying box had not been used for a while.

As Sven Jacobsson 9:23 PM started a new round, he saw fire in the splint hall.

The Police and fire protocol verifies fire in a polishing drum at the drying box on the west side of the splint hall. In the newspaper it was said that fire had been seen in a slot of one of the drying boxes, in, or close to, one of the drying boxes in the splint hall. Fire had also been seen from outside coming out of an airshaft over the splint hall roof.
As the fire alarm was registered at 9:25 PM, the Växjö fire brigade and reserve corps turned out with the tool wagon, after that with the mechanical ladder, and finally with the small and the larger fire steam engines. At 9:28 PM, six firemen with a foreman were in place. Fire Master Zsar expressed his opinion that the fire already was impossible to extinguish or to subdue. The big lathe-hall was on fire.

At 9’40 PM alarm is given to the 40 firemen that are as reserve at the regiment I11, and as it is risk for a large fire, order is given at 10PM to 700 men of the regiment I11’s forces to help. The regiment’s forces are used to cordon, keep guard, demolition and lay out fire hoses. As a southwest wind threaten the blocks in the city, two men were ordered to protect each yard.

At 10:25 PM, the police began to alarm the 491 men of the public fire brigades by chiming church bells. As the fire reached the northwestern part of the factory, twelve fire hoses of a total length of 2000 m were used to protect the main building, and other buildings,
especially the adjacent warehouses containing matches and chemicals. The Växjö waterworks were pumping at maximum capacity level and delivered 4 m$^3$/min.

The cathedral bells accompanied by chemical explosions awoke people, big crowds hastened to the fire site as the fire could be seen and heard far away. Very heavy rains of sparks flew over the city, and burning pieces of wood fell down more than 3 km away.

**WHAT CAUSED THE FIRE AT WEXIÖ MATCH FACTORY.**

At 1:00 AM on May 31, the fire was under control, and at 7:00 PM the fire brigade’s extinguishing of the fire was finished. The public prosecutor held during the day a police interrogation about the fire. Earlier cases of chemical self-ignition were known and was considered the reason of the fire. The main personnel at WTF and of the fire brigade were asked about observations during the fire and their opinion about the possible reason of the fire. Some evidence pointed at heating of a bearing in the roller, but it could not be proved.

No chemicals that could have caused the fire were to be found. The investigation was closed without finding out the reason for the fire. (VLA FSTF F:6)

In the evening of the 1st of June, at 9:12 PM, the fire alarm sounded again! The fire brigade and the reserve corps turned out with the mechanical ladder. Amorphous phosphorus stored in a cellar had ignited. During removal at the big fire the day before, tins containing red phosphorus were damaged, leading to spontaneous ignition. The fire was extinguished with a fire hose present in the cellar. (VKA BS Di)

In June 1922, WTF made its monthly factory inventory list for May 1922. (VLA JoV) All raw materials that were destroyed by the fire, or for some other reason should not be recorded seem to be designated “other use”. The inventory list takes up: alum, aniline dye, antimony trisulphide, asbestos, aulphore acid byrat, auramin, manganese ore, campeche tree, carbon black, caput mortum, chalk, potassium chlorate, chrome yellow, dextrin, fuchsine, glass
powder, gum arabicum, gum dragant, kieselguhr, lime, paraffin, pedoxin, phosphoric acid, phosphorus, photogene, pumice, quartz, red colour, resin, rhodamin B/G, sulphur, sulpofosfit, sulphuric acid, Glittermalm, tin, zinc plate, zinc white

The manager at WTF, Knut Johansson, noted down all known, all older recipes and all the recipes used at the time of the fire. (FOAK WTF)

The Skandia insurance company paid out SEK1 317 275 for the fire damage (VLA FSTF F:6)

**Chemical investigations**

Between 1919 and 1922, the consumption (in kg) of different types of red phosphorus at WTF was as shown in the table below. (VLA JoV EVIIIb)

<table>
<thead>
<tr>
<th></th>
<th>jan</th>
<th>feb</th>
<th>mar</th>
<th>apr</th>
<th>may</th>
<th>jun</th>
<th>jul</th>
<th>aug</th>
<th>sep</th>
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<td>Swedish</td>
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<td>516</td>
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<td>400</td>
<td>100</td>
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<td>400</td>
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<tr>
<td>English</td>
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<td>380</td>
<td>465</td>
<td>355</td>
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<tr>
<td>German</td>
<td>350</td>
<td>200</td>
<td>260</td>
<td>305</td>
<td>315</td>
<td>220</td>
<td>225</td>
<td>280</td>
<td>220</td>
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<td><strong>1922</strong></td>
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<td>English *</td>
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<td>-150</td>
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<tr>
<td>German **</td>
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<td>170</td>
<td>235</td>
<td>-500</td>
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<td></td>
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</tbody>
</table>

* -350 kg designated for "other use", * -150 kg sold to Vetlanda. ** -500 kg was returned

On June 13, 1922, STAB’s Purchase Department informed about the “German phosphorus order No. 97” from the Chemische Fabrik Griesheim-Elektron in Frankfurt am Main. (VLA JV EJ)

Of 100 tins distributed on March 23 were 51 tins returned May 6 and 30, for investigation in Germany. The acidity – due to oxidised phosphorus – was determined by titration with 0.1 molar sodium hydroxide. In 33 tins the acidity varied between 1.1 - 3.5 ml 0.1 M NaOH / gram.

On June 16, 1922, it was urgently required that tins containing inferior phosphorus should be hermetically sealed by soldering and stored separately.

On June 28, 1922, was in “Circular 35” the Griesheim-Elektron report presented about the problems experienced with different types of red phosphorus.

The diagram shows the acidity of various phosphorus brands as a function of air exposure time. In practice their disposition to get acid in relationship with air. The test result is expressed in curves as a specification of the investigated sample. From the curves we conclude that the washed phosphorus oxidise considerably faster than the unwashed.
The investigation show that the Swedish phosphorus had the lowest primary acidity, i.e., the lowest degree of oxidation. While the Italian washed, exhibited the highest degree of oxidation.

The investigation left no results about the general quality of the phosphorus, such as as degree of transformation, grain size, ignition, etc. It only dealt with the relative degree of oxidation when kept in and outside package. (VLA JoV EI-502)

On July 25, 1922, STAB’s Purchase Department informed about “German phosphorus order No. 409” comprising 5000 kg of phosphorus in boxes of 5 kg that had arrived to Gothenburg. 2000 kg were test-distributed with 500 kg to each: the Uddevalla factory, the JT and JVT in Jönköping, and to the Vulcan factory in Tidaholm.

The factories, were asked to control the phosphorus quality rigorously before use, reported;

Uddevalla 20/7: Every German box is investigated, we will report every remark.
JT 22/7: The batch contents <0,5% acid, we will report after use.
JVT 12/7: Phosphorus is clean enough from acid and of good quality
Vulcan 24/7: Phosphorus contains white phosphorus and take up much more moisture than English phosphorus; we would rather be excused to use the phosphorus in question. (VLA JoV EI-502)

Some WTF correspondence for the year 1922, both before and after the fire, is not found in the archive-files. Missing are also Circular that Torsten Jung in Jönköping had in his confidential “C-file” as Circular: 208, 248, 289, 290, 294, issued between 1923-30. (VLA JoV EVII)

In 1934, JoV Match Co. issued “Circular 357” to all the STAB factories. It deals with an investigation of “Fires when tins with red phosphorus were emptied”.

The investigation was undertaken in 1933 after a fire occurred in a red-phosphorus tin in the Kalmar factory. From reports from other factories it was concluded that fire had occurred at many factories, but with long intervals.

<table>
<thead>
<tr>
<th>Factory</th>
<th>Time</th>
<th>At work with</th>
<th>Fire ignition course</th>
<th>Cause</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jönköping</td>
<td>1926</td>
<td>Emptying</td>
<td>Phosphorus dust</td>
<td>Bad phosphorus</td>
<td>English</td>
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<tr>
<td>Jönk o Vul</td>
<td>1914</td>
<td>Emptying</td>
<td>Phosphorus dust</td>
<td>Friction</td>
<td>German</td>
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<tr>
<td>Jönk o Vul</td>
<td>1926</td>
<td>Emptying</td>
<td>Phosphorus dust</td>
<td>Friction</td>
<td>English</td>
</tr>
<tr>
<td>Kalmar</td>
<td>1933</td>
<td>Emptying</td>
<td>Ignition explosion</td>
<td>German</td>
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<tr>
<td>Lidköping Norra</td>
<td>1931</td>
<td>Opening</td>
<td>Ignition as opened</td>
<td></td>
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<tr>
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<td>Unknown</td>
<td>Unknown</td>
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<td>Uddevalla</td>
<td>1929</td>
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<td></td>
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<td>Unknown</td>
<td>Opening</td>
<td>Hit against tin</td>
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<tr>
<td>Västervik</td>
<td>Years ago</td>
<td></td>
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</tbody>
</table>

Experience from the factories tells that tins had to be emptied with highest caution, and the emptied tins should be handled with outmost care.

As an unopened tin in Kalmar was investigated, it was found to contain phosphine (phosphorus hydrogen), but no white phosphorus was found. This is known from English phosphorus tins. The phosphorus hydrogen could possibly cause an easier ignition.

The opening rules were changed: A tin opening tool for cutting off the lid should be added to the homogenising mill in the composition room in order to minimise shaking of the tins as they were emptied. The tin opener should be moistened with water before use. The top of the
tin should be cleaned before opening, and moistened. The worker should use leather gloves and a gas mask. When the lid has been removed, the tin should be left open for a maximum of 6 hours before the tin was emptied. (VLA JoV EVII)

**PHOSPHORUS DISPOSALS “BACK IN THE LIGHT”**

As in 1973 Firemaster Per-Olof Landström at the Nässjö fire brigade turned out with truck No. 8 to the Anneplast wall-paper factory on the site of the old Anneberg match factory, he found the ground in fire. (Nässjö brandkår, 1973 report 164)

During excavation the smell of garlic was perceived, a sure indication of fosfin, that the phosphorus in the old residue selfignited when exposed to the air. (STAB)

In 1911, the production of phosphorus matches ceased at the Anneberg match factory. It has been told that big, empty barrels without lids were pressed down into the wet ground. Phosphorus was then poured through the barrel as through a tube, and sunk in the ground. Finally, sand was shuffled after the waste. (STAB) The phosphorus was disposed of in this way because of the intensity it causes when burned in the boilers and the risk of damaging them.

As in 1995 the county authorities examined the ground and water around the old match factory. The total phosphorus in Svartån stream, was upstream of the factory 0,066 mg/l, downstream 0,17 mg/l. The reason the phosphorus leakage were not found. (Jönköping county)

**Possible disposal of phosphorus from WTF**

In February 2001, an environmental jurist told me about a person, who between 1940s and 1960s had seen how, after a heavy rainfall, white smoke came up from the ground where once the Växjö pond was situated. This is an obvious indication that the ground holds white phosphorus. As the ground was to be excavated, the authorities in Växjö were informed of this fact, but no environmental investigation of the site was undertaken.

**Excavation of the old Växjö pond.**

The contractors of the enlarged library building never excavated the ground on the told suspicious points. Only a higher value of phosphorus was registrated in the groundwater during excavating.

![The Växjö library in 2001.](image)
**Present status**

The disposed waste from the match factories were long forgotten when present days’ environment inventories are made; the disposal activities were finished a century ago. Today old match factory sites could be affected by match, sites that today are situated in town centres.

The Swedish phosphorus decree of 1870 stipulated that phosphorus waste should be burnt.

In the production, white-phosphorus waste was kept in buckets and covered with water. These buckets were as a rule emptied in marshy ground, because burning in the boilers was too intense and the risk of boiler damage high.

Water from the washing and cleaning of the phosphorus working rooms, which was made every two weeks, should be thrown in a deep, separate well (Swe: Brängrop, i.e., fire pit). Was there water in these wells or not when they were used? If there was, the white phosphorus in the discarded composition can be kept anaerobically in the bottom sediments for a very long time. (FOA-Rapport-00-01569-222)

If there was no water furthering an anaerobic condition, the white phosphorus was slowly oxidised in contact with air.

Information about the waste is in the archives. After finding out the details of the individual disposal system used and their present conditions, environmental remediation actions can start.

**WTF waste statistics based on 1891 match recipes**

The 1870 phosphorus decree stipulated how to handle waste and water from the factories.

Between 1868 and 1913, WTF consumed approximately 85 tons of white phosphorus.

In the 19th century, the groundwater level at the site for WTF was such that a deep wash water well, if and wherever it was situated, must have contained groundwater. Assuming that 0.5% of the white phosphorus was thrown out with the wash water, the ground where WTF’s wash water well is situated could hold 400 kg P₄. If we assume that 3% white phosphorus was disposed, the Växjö ground could hold as much as 2.5 tons P₄.

In 1913, when WTF discontinued its production of phosphorus matches, a disposal of the remaining white phosphorus could have been made. In 1922, red phosphorus tins turned out to be contaminated with white phosphorus. After the fire at Wexiö Match Factory (WTF) 1922, red phosphorus tins self-ignited after been damaged under removal during the fire. According to available factory statistics, we are probably dealing with 70 tins of 5 kg each.

If we assume that this is the secret transport made in the 1920’s, 350 kg of white phosphorus-contaminated red phosphorus could have been disposed in the marshy ground in the east part of the Kronoberg county.

In the 1920’s and 30’s, red phosphorus tins have self-ignited as they were opened, or afterwards, and caused unexplainable fires at Swedish match factories. Investigations made found phosphine in such tins. This poisonous gas might have facilitated the ignition.

**The environment**

It is difficult to judge, identify and estimate possible environmental consequences. It is imperative to look through the archives for information. The suspected areas should be investigated with modern techniques, and cleaned. It is vital to ensure that the suspected sites and transported materials won’t be harmful to people or the environment now or in future.

Recently I found an excavator digging a 3 m deep pit in Lärkgatan, where the Wexiö Match Factory (WTF) once was located. As digging, a white cloud came up from the ground enclosing the excavator, smelling strongly. Going down into the pit, the workers found the ground full of white-gray nearly burning ground material.
The workers led me to find a person that 1983 worked with excavation of the roads in the same area. Several phosphorus fires had then started when it was dug in Biblioteksgatan. The crossing of Biblioteksgatan and Lärkgatan is a waste disposal site.

The Wexiö Match Factory (WTF) story is not yet finished, the last chapter will be written as on the other places were phosphorus has been handled in the past.
INTRODUCTION

This project on Energy Recovery was established in 1990 by a Swedish initiative as an integrated part of a new committee when CEN (Comité Européen de Normalisation) founded and structured its Technical Committee TC 261, Packaging. An incentive for all this came from EU, which had started a preparatory work for a Directive on Packaging and Packaging Waste.

TC 261 was organised with four subcommittees (SC), each of them with several working groups (WG). The total number of WGs was 25. In TC 261/SC, 4 different WGs were organised:

- Terminology, symbols and LCA
- Degradability and composting
- Material recovery
- Energy Recovery

- Prevention
- Reuse
- Heavy metals and other dangerous substances
- "Umbrella"/General approach

During the first years of discussions on a draft directive, the document was an item of discussion at each meeting and many comments and proposals were sent to the Commission, i.e. DG XI (now DG Environment). The eighth draft was completed on the 20th of December 1994 as Directive 94/62/EC on Packaging and packaging waste (Ref.1).

The environmental aspects are very important parts of the Directive, and in 1996 the Commission mandated work on Environmental packaging standards to TC 261 and its SC 4.

The results of this work were accepted gratefully by the CEN Members, but a few EU Member States reacted negatively. The solution of this impasse ended with a second mandate in 2001, a mission CEN/TC 261 now has fulfilled.

PREVENTION OF THE ENVIRONMENTAL IMPACT OF PACKAGING WASTE

Requirements specific to the manufacturing and composition of packaging are given in the Standard on Prevention by Source Reduction (Ref's 2, 3 and 4). All packaging, including that for which energy recoverability is claimed, has to fulfil these requirements. This means that the packaging functional unit contains a minimum amount of material. In addition, the amount of heavy metals and other...
hazardous and noxious substances is minimised, which has implications for the environmental impact of the energy recovery process.

**OPTIMISATION OF ENERGY RECOVERY**

The energy recovery standard provides the requirements for a packaging to be recoverable in the form of energy. The first Commission mandate asked for a minimum net calorific value to allow optimisation of energy recovery.

Optimisation of Energy Recovery from packaging waste involves the overall system including properties of packaging, waste collection systems, preparation, and storage and energy conversion to provide useful energy as shown in Fig.1. Some steps included in the overall system are not related to packaging itself. Combustion plants and the handling of residues from combustion, for example, are subject to specific regulation.

![Diagram of Energy Recovery Process](image)

**FIG 1** Optimisation of Energy recovery from packaging waste

To allow the optimisation of energy recovery from packaging waste, all steps in the recovery route must, however, be considered. This means that the consideration of energy recovery of packaging waste should include not only packaging materials and packaging design, but also the handling of packaging waste and recovery of the energy, i.e. the generation of heat into the flue gases of the furnace and recovery of the heat from gases into the boiler.

The use of this heat is, though, important for the optimisation of energy recovery, outside the recovery route and cannot be influenced by measurements taken by the packaging manufacturer. The standard covers the route from packaging design to the generation of calorific gain.

Figure 1 illustrates the two possible routes for energy recovery of packaging waste. The upper route is conventional incineration of waste. The lower route includes separate collection of packaging waste, preparation of a fuel with specified properties, and recovery of the energy, either as a mono-fuel or in co-combustion with other solid fuels.

For incineration of waste, the Waste Incineration Directive (Ref. 5) regulates the emissions from the plant. For solid fuel combustors, the fuel derived from packaging must meet the specifications of the actual plant.
The standard EN 13431:2000 (Ref. 6a), produced under the first Commission mandate, states that the principal requirement for packaging to be recoverable in the form of energy is that it is combustible under ordinary conditions. The requirement of optimisation of energy recovery was addressed thermodynamically by introducing the concept of calorific gain.

To allow optimisation, packaging should be capable of providing calorific gain. This means that the net heat of combustion, \( q_{\text{net}} \), of the packaging shall exceed the energy required, \( H_a \), to adiabatically raise the temperature of its combustion products, residues and excess air to the required temperature:

\[ H_a - q_{\text{net}} > 0 \]

The conditions specified are those for waste incineration, as regulated in Reference 5, i.e. an ambient temperature of 25 °C and a final temperature of 850 °C at 6 % O\(_2\), assuming negligible unburned losses and steady state conditions.

All organic materials and most multi-material, lightweight packaging, containing a major amount of organic material fulfill Equation 1.

The calorific gain concept is a general condition, set for the ideal adiabatic case and independent of packaging material. In real energy recovery processes, there are always heat exchange with the environment and, of course, thermal losses. The available thermal energy in the real processes is, however, larger than the calorific gain of the ideal calculations, even when the losses are considered, due to heat recovery of the hot flue gases.

Waste-to-energy plants are constructed to recover energy from MSW. \( q_{\text{net}} \) of mixed MSW is of the range of 8-10 MJ/kg. Separate collection of wet bio-waste for organic recovery increases the energy content of the waste-to-energy fraction. The design range of modern incinerators is therefore 11-13 MJ/kg or even higher. This has nothing to do with optimisation of energy recovery but is required to adapt the incineration process to the available waste feed, in order to avoid a thermal restriction to the incineration capacity (t/h) of the plant. Packaging waste, being a mixture of used combustible packaging, represents the energy-rich fraction of the waste stream.

From studying real combustion processes it is seen that calorific gain is obtained in practical combustion processes for fuels having calorific values even as low as 3-5 MJ/kg. The important factor is the optimisation of the combustion process, i.e. the adaptation of the fuel to the combustion process (or vice versa). An increase of the calorific value of the fuel does not in itself lead to optimisation (Refs 7 and 8).

**THE MINIMUM NET CALORIFIC VALUE**

A thermodynamic equation did not, however, satisfy the Commission, who demanded a numerical figure of the minimum net calorific value.

Based on the findings of the energy content of packaging components and packaging functional units fulfilling the concept of calorific gain, a figure of the lowest net calorific value for a “worst case” packaging material was derived.

Fig. 2 is a plot of the calorific gain as function of \( q_{\text{net}} \) for packaging and packaging materials from Table 1. The line is the extended line of the mean values calculated according to the least square method and extended to \( q_{\text{net}} = 0 \). The extrapolation shows that calorific gain > 0 when \( q_{\text{net}} > 2 \) MJ/kg. Taking the 95 % confidence limit into account, the theoretical minimum value is < 2.5 MJ/kg.

To allow optimisation, i.e. taking maltreatment of the fuel, residue handling and eventual extra transportation into account, the practical, real value, \( Q_{\text{net, min, real}} \), should be larger than the theoretical value, \( Q_{\text{net, min, theor}} \). Applying a safety factor of 2, commonly used in design and construction of industrial processes, the practical, real, minimum value is set to 5 MJ/kg. For a \( Q_{\text{net}} \) of 5 MJ/kg, the calorific gain is \( \approx 2 \) MJ/kg, and the calculated available thermal energy in a real process 4 MJ/kg or more. Even when the energy consumption for additional transportation and handling, flue gas cleaning and residue handling are taken into account, the available thermal energy exceeds the energy consumed by these operations.
INORGANIC CONTENT OF PACKAGING

The requirement of calorific gain limits the amount of ash forming substances, since inorganic constituents, except aluminium, give a negative contribution to the calorific gain. The general requirement of provision of calorific gain may, however, allow material combinations that would not be considered energy recoverable, such as a combination of plastic and metal packaging or organic coating applied to metal packaging. Although this packaging may very well enter the MSW stream for incineration and be recovered as material out of the slag, they should not be considered energy recoverable. Therefore, the content of inorganic components is limited to 50% by weight. Inorganic constituents, such as clays and lime, may even be beneficial for the combustion process, and are allowed at higher concentrations, provided $q_{\text{net}} \geq 5$ MJ/kg.

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Requirement: $q_{\text{net, min, real}} \geq 5 \text{ MJ/kg}$

Figure 2. Calorific gain as function of $q_{\text{net}}$ for constituents, components and packaging from Ref. 6b. The line is calculated according to the least square method and extrapolated to $q_{\text{net}} = 0$. (Note: the three points well above the line represent examples containing more than 40% aluminium (by weight). Thermodynamically, aluminium does not behave like organic materials, and these data are excluded from the calculations.)
ENVIRONMENTAL ANALYSIS OVER
THE SWEDISH DEMILITARIZATION INDUSTRY

Emma Nehrenheim
Department of Public technology, Mälardalen University

ABSTRACT
A close examination of Swedish ammunition disposal reveals, among other things, that the
use of resources and energy, not the least in connection with transportation, seems to be an
often neglected environmental impact issue. Being international in nature, the problems
connected with these issues can be solved only by international co-operation.

The Swedish Defense Material Administration (FMV) is a state agency that can influence
consideration given to environmental issues. In connection with tender inquiries on open
ammunition disposal, FMV can define a number of environment-related demands. One such
demand has been studied at Mälardalen University. It was found that the environmental
aspects of transportation are as a rule neglected in an overall assessment. Road transportation
of ammunition as well as handling at the disposal site are indeed important issues of the entire
disposal process.

Today’s main reason for the ammunition industry to pay due attention to the eventual dis-
posal process, is that recovery of materials in connection with ammunition disposal considera-
bly reduces the environmental impact. Furthermore, doing business with recovered materials
is a profitable side effect. Another side effect of careful planning of this type of processing is
the positive influence on human health and biological diversity.

INTRODUCTION
This paper is a result of a undergraduate thesis project done in co-operation between
Mälardalen University and KCEM. The purpose is to describe recycling and destruction of
ammunition in Sweden and how the environment is effected by this. Environmental concern
in industrial processes, including the ammunition industry, is a high priority today. The
purpose was also to find the most important parts in the process cycle concerning
environmental assessment and sustainable development.

Swedish ammunition is phased out when for some reason it has become unsafe to use.
Defects from production can be the cause but most commonly it is when ammunition has
been stored for a long time and gone out of use due to safety reasons. Most of the ammunition
stored in Sweden today is more than 50 years old. Dumping in lakes and open burning have
been common methods for disposal of ammunition through time. Dumping has been
prohibited since 1971 and there is likely to be a prohibition against open burning as well. (Hörnström, 1996)

When analyzing the environmental assessment of a product, it is important to study its complete lifecycle including energy consumption and impact on nature related to transportation. The different steps are unequally important depending on the design of the process steps. One basic idea could be that the relevance of the improvement depends on the use of fossil fuel and discharge of globally effecting pollutants.

RECYCLING OF AMMUNITION IN SWEDEN

The only company recycling ammunition in Sweden is Vingåkersverken. Most of almost all the ammunition arriving at Vingåkersverken is recycled or destroyed. Recycle of material is the primary method in Vingåkersverken. This not only offers avoidance of the toxic flue gas, which results from incineration, but also allows reuse of resources which otherwise would have been lost. Today, reuse of material is the most acceptable method for recycling of ammunition but some parts of ammunition is still combusted when there is no known profitable way to reuse it. For sea mines and other large items, the most important step in the recycling process is open burning of left over explosives. This is the only step in the end of life cycle of ammunition where the material is not reused. This step is considered a problem at Vingåkersverken (Timner, 030520).

TNT is an environmental problem. Samples in the area surrounding Vingåkersverken show signs of TNT. However these levels are under the guidelines set by The Swedish Environment Protection Board. This shows that the purification is effective in the water treatment process of the out going water from the process of melting TNT.

The environment is also effected by the use of energy. Vingåkersverken uses oil as an energy source for all its processes. Oil is a fossil fuel. The increased use of fossil fuel over the world has led to a discussion on how to replace it with other more sustainable fuels.

The discharges from open burning of left over explosives in the ammunition have been valued as the most significant of the steps of recycling in Vingåkersverken.

THE COST OF ENVIRONMENT PROBLEMS

The Swedish government has established that the environmental problems are expensive for Sweden. These costs are represented by worse human health and biological diversity but also concrete costs like production losses and waste of material. Every step of the lifecycle involves use of resources which can be minimized with recycling and development of markets of reused products and material. (SNV 5177, 2001) The government asks in a proposition (2000/10:130) for a method of evaluating the environmental costs together with the social and economical issues and suggests three strategies. One of these means a more efficient use of energy, resources and transportation which aims to contribute the achievement of the goals for acidification, eutrophication, fresh air and climate.

AMMUNITION AS HAZARDOUS WASTE

The view of waste is two sided. Waste is balancing on the edge between being an environmental problem and a resource where the technical development is crucial. The Swedish Environment Protection Board has in report 5225 put the responsibility for the different parts of the lifecycle on the different actors. The government has the overall responsibility for leading the country towards sustainability within production and consumption. Use of resources is considered the main problem because it gives rise to
discharges of heavy metals and influence on flora and fauna. The Swedish Environment Protection Board has also agreed that the transportation of goods has a significant part in a products lifecycle and advocates this trend must be broken though a co-operative work between different countries. In the report, The Swedish Environment Protection Board suggests that the status of the environmental questions in EU are raised to the same level as the free trade. (SNV 5225, 2002)

Economical means of control is a way for authorities to give signals to the surrounding community that environmental concern is important. With help from the law, authorities can control the power of the market to influence the actors in favor for the environment. Taxes or requirements for technical improvements like catalytic converters in cars are examples of this. Companies with high environmental performance can influence their suppliers and cooperation partners with higher demands. Swedish Defense Material Administration is a state agency with a high responsibility for the signals given to surrounding actors. They have in their purchases very large possibility to influence the environmental concern within the framework for disposal of old ammunition. In one of the enquiries a formula was formed to illustrate the connection between price and environmental concern. They have weighted the environmental concern as 60 % of the total judgment and the price as 40 %. In this case environmental concern means material reuse (Anbudsinfordran FMV, 20020715). While costs in transportation is included in the price section, no concern is taken for transportation in the environmental part of the formula.

**TRANSPORTATION AND OPEN BURNING OF LEFT OVER EXPLOSIVES**

After having studied earlier literature and interviewed experts in the recycling process it was possible to establish that the open burning of explosive contaminated ammunition parts is the step in the recycling process with the highest environmental assessment. This led to a comparison between the open burning and the transportation of goods since the transportations can be expected to have a large environmental assessment. For the comparison, an internet based calculation program developed by the goods transportation industry is used. This model is called NTMcalc and is used by the transportation business to find out the environmental assessment when different alternatives are compared. The model is not based on new fact but is a compilation of data from different actors like for example Volvo LV and Scania (NTM’s homepage 030512).

The trucks can take 40 tons but normally around 37-38 tons are loaded on each load. Exceptions are made when the ammunition contains large amounts of explosives or if the store does not contain a full load. (Elfer, 030514). The emissions are allocated on the weight of a sea mine to receive data of emissions from each sea mine to use in the comparison.

Ammunition is transported by truck from the stores all around Sweden. Other means of transportation could give a different result. For instance train is considered a more environmentally friendly option.

One sea mine (F31) is used in this comparison. Note that the section chosen here is 200 km, it is relevant to expect longer distances when ammunition is transported.
This comparison (Figure 1) shows the discharges of some substances. The open burning, which is the most critical step in the process of recycling, has smaller discharges compared to transportation of the same mine. Acidic substances are the most obvious impacting in the comparison but it is easy to see that also carbon discharges is important in transportation, especially when the distance is long.

**REUSE OF MATERIAL FOR MILITARY PURPOSE**

Methods for reuse of material for military purposes have been studied in Sweden. Today all recycling of ammunition is done for the civil market which involves an economical decrease. Military reuse could increase the number of buyers but today the only produced ammunition is from raw materials. No reused material is ordered by the Swedish Defense Material Administration because of problems with quality guarantee. (Hägvall, 2002)

**DISCUSSION**

The adjustment into a more environmentally acceptable society means that a preventable work has to be done in several areas.

Discussion about an adjustment to a more environmental friendly process will in some cases be about the question of sending material for recycling far away even for a small number of percentage recycling. Transportation with truck means emissions while increased recycling promotes other kinds of sustainability. Valuation, between the environmental assessment in transportation compared to the possible environmental profit in higher percentage reuse of material, is complicated. The first case is about waste and resources while transportations primary influences the climate. These are two environmental effects that can not be compared to one another without making values grounded on subjective opinions (Söderbaum, 1986).

An discussion must be held about the environmental issue. The profit in more environmental preferable solutions in ammunition recycling must not cost to large assessment on the global environment in largely increased discharges of greenhouse effect related gases. One problem is also transportation of old ammunition as hazardous waste because of the risks.
it results in. Making an environmental assessment comparing these transportations with the degree of recycling involves a personal judgment which is also subjective.

**FUTURE STUDIES**

Old ammunition is treated as hazardous waste in Sweden which means handling ammunition has to be done with consideration to the waste laws. This is not necessary the case in all European countries why the regulations in handling ammunition and the guidelines in the processes can be different in different countries. It would be interesting to see if Swedish laws prevent the possibilities to develop Swedish processes or makes it easier.

It is interesting to determine the actual cost of emissions on the environment as production losses, increased corrosion, health effects etc, and we will work on this subject. Alternative, innovative recycling methods and alternative usage of recycled materials is another area of specific interest, to make the recycling as cost effective as possible. Emissions from different destruction processes will also be studied more in detail. System aspects and the lifecycle perspective including factors like considerations of recycling already in design of ammunition is of importance.

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DESTRUCTION OF CONVENTIONAL AND CHEMICAL MUNITIONS IN A DYNASAFE STATIC KILN

Johnny Ohlson
Dynasafe AB, SE-691 80 Karlskoga, Sweden

ABSTRACT

The Static Kiln is a hot detonation chamber developed by Dynasafe AB to be used for destruction of conventional and chemical munitions. The destruction of munitions is carried out at high temperature under gas-tight condition. The Static Kiln has been used for destruction of small arms ammunition, antipersonnel mines, incendiary munitions, white phosphorus, smoke munitions, stockpile and nonstockpile as well as chemical munitions.

An overview will be given in the presentation of the design principles of the equipment, the destruction process, examples of the remains of the munitions, and experience and lessons learned from many years of operation of different Static Kilns.
CREATIVITY – A POWERFUL TOOL IN CREATING NEW ORDER FROM CHAOS. A BRIEF RETROSPECT OF ALFRED NOBEL’S IDEAS AND INVENTIONS

Hans Eriksson
Katrineholms Patentbyrå AB, SE-641 21 Katrineholm, Sweden

ABSTRACT
Alfred Nobel is still one of the most well-known Swedes ever, in spite of the fact that he has been dead for more than 100 years. In the autumn when we Scandinavians are waiting for the light and sun to return we are reminded of Alfred Nobel’s spirit and work in the Nobel Prize ceremony. We think we know Alfred Nobel and his work pretty well, but the process to fully understand a genius is slow and, in fact, requires entrance to, or at least a glance into, the same world of ideas as he once created. We can do that by studying Nobel’s life and work, and in this presentation I want to comment on his patents in different technical fields in an attempt to explain why he was capable to do a lot more than “just” invent the Dynamite.
REMEDIATION OF POLLUTED SEDIMENTS THROUGH UNDERWATER DEEP FREEZING

Susanne Rostmark and Sven Knutsson
Luleå University of Technology, SE-971 87 Luleå, Sweden

ABSTRACT
Artificial ground freezing (AFG) is a well-established technique first practised in South Wales in 1862. Since then many different temporary and permanent applications have been developed. AFG is mostly used in tunnels and for stabilising excavations, but there is an increasing interest in using AFG for environmental protection and for using freeze/thaw cycles for remediation of contaminated soil. Freeze dredging is a novel dredging technique developed at Luleå University of Technology in co-operation with industrial partners. The contaminated sediment is first stabilised by freezing, and then the frozen sediment is lifted up above the water with a minimum of disturbance of the surrounding soil. Full-scale field tests have been performed with very good results. It has been hypothesised that underwater freezing can be used also for removal or radioactive material, fragile containers with hazardous content, and ammunition.

This paper describes the basic principles of the technology and lessons learned from the full scale tests. It also deals with considerations necessary for designing a system for underwater freezing of different materials.
RISK ANALYSIS AND RISK ASSESSMENT IN THE PRODUCTION OF ENERGY FROM WASTE AND BIOMASS FUEL

Bengt Sahlin
Ragn-Sells Miljökonsult AB

BACKGROUND

During the 1995-96 fiscal year, the National Board of Occupational Safety and Health and five Inspection Districts have conducted a project entitled *Work environment aspects of the ecocyclic management of residual products and waste*.

The purpose of this project has been to develop within the National Occupational Safety and Health Administration a consensus view of matters relating to work environment aspects of the ecocyclic society. The aim has been to promote a course of development in which work environment objectives are harmonised with external environmental targets. This means preventing work environment problems resulting from the ecocyclic adaptation of residual products, by translating our knowledge into action, so that it will exert a beneficial influence conducive to the prevention of work injuries and accidents.

Refuse collection and disposal employees have by tradition been prone to many kinds of work injuries. Their injury risk is about three times that of working life in general. Refuse collection workers are above all prone to ergonomic injuries and accidents during the collection of refuse. Now that container collection is being introduced and work is in progress to reduce the element of stress in this branch of employment, we can hope for a reduction of work injuries. At the same time, unfortunately, one finds that containers are tending to grow larger and more unwieldy, which may offset the positive trend. We can also observe an upsurge of microbial problems among refuse collection personnel.

New jobs are being created with the introduction of the ecocyclic society, e.g. in the pre-separation sector. We have reason to believe that these jobs will create major work environment problems in the next few years.

Among other things, the project participants noted that employees with functional impairment and ALU (work experience scheme) workers were being used for preseparation work. It was also observed that the design of the actual pre-separation process was in need of review. The physical environment of work facilities also needs to be improved.

By insisting on a good working environment, municipal authorities can exert partial control over the working environment provided by their contractors. In order, therefore, to ensure the quality of contracted refuse management services, the municipality should take care that the contractor’s working environment is also included on the negotiating agenda. In
addition, the National Board of Occupational Safety and Health must work to ensure that similar demands are made on material companies, in their procurement of services, as regards the working environment of their contractors.

The National Board of Occupational Safety and Health finds it important that the National Environmental Protection Agency should also take work environment aspects into consideration in its documents on the ecocycle and waste management questions, since those documents often form the basis of policy decisions by the Ecocyclic Delegation. The Board finds this important, because ecocyclic questions are dealt with by the Ministry of the Environment and work environment questions by the Ministry of Labour. The Board, then, wants ecocycle questions to be viewed in a more comprehensive perspective than that of the external environment alone.

The Occupational Safety and Health Administration has also given priority to work connected with ecocyclic adjustment in its operational planning.

In the field of waste handling it has been stated by the authorities that collection, handling and separation of non hazardous waste has more than 3 times more reported accidents than average. Reported occupational diseases are double compared with the average.

In the wood industries where most of the biomass fuel is produced, statistics show 2.5 times as many reported accidents relative to the average. The reported occupational diseases are slightly higher than average.

The Swedish government has announced several new laws to reduce the cost of sick leave and sick pensions because of the rapid growing and large cost for this. The work environment authority has also set up several new codes of practice (Provisions/Ordinance) demanding that employers make risk analyses and risk assessment. The latest is AFS 2003:3 Arbete i explosionsfärlig miljö (Work in an explosive environment)

Looking at the fires happening in the production of energy from waste and biomass fuel it can be difficult to get all the specific statistics but several explosions and fires have occurred in the last 20 years in, for example, Nässjö, Västervik, Södertälje, Umeå, Ärjäng. Many fires have been self ignited but others have been caused by electrical short, welding and overheating of equipment. The largest fires in sawmills and pellet factories during 2000-2002 cost the insurance companies more then 195 million SEK (21 million Euro). The total cost of all fires in Sweden for year 2002 is among the highest ever according to statistics over ten years. The cost of the largest fire 1998 in Västervik’s production unit was over 30 million SEK.

The Swedish government is discussing a new law to replace the law of rescue service (Räddningstjänstlagen). More responsibilities will be placed on the owner of real-estate, buildings and production units with regards fire inspections and documentation as well as for reporting fire protection solutions to the local municipality and fire brigade.
RISK ANALYSIS AND RISK ASSESSMENTS

There are many different methods for risk analysis and risk assessment being used in Sweden today. Most of these methods have their origin at technical universities both in Sweden and abroad. The methods have then been used to do research in different types of industries and been adapted to specific tasks or branches.

The methods have then been published by different organisations or publishers such as Prevent, The Association of Swedish Engineering Industries.

The interesting thing is that the Work Environment Authority has many codes of practice (Provisions/Ordinance) with requirements for employers to do risk analyses and risk assessments but no recommendations for methods. The only requirement is that the risk analyses and risk assessments are done systematically and using a recognized method.

Looking upon the possibilities for preventing not only accidents and occupational diseases but also fires, there is a need for using different methods and also different experts when doing risk analyses and risk assessments for the production of energy from waste and biomass fuel.

Furthermore, waste and biomass fuel have changing chemical and physical parameters depending on the producer, the raw materials, the tax on different waste and fuel etc. When these changes are done there is very little done so as to foresee any new risk when handling the “new” waste and biomass fuel.

For example, Igelstadsverken, Södertälje was designed to use coal as the fuel. After some years, the main fuel is biomass fuel and waste. The transport and handling equipment is still the same. The new chief of production was only in charge for a short time when a large fire started in the storage for bio fuel with a large loss of production, equipment as fuel. The chief of production has now decided to make a risk analysis and risk assessment. There are some difficulties for companies who bid for such consultancy work. Which methods and what kind of experts are requested? Few consultancy companies have experts in the fields of working environment, chemicals, environment and fires.

The cost will probably be high for a total risk analysis and risk assessment including safety of machinery, ergonomics, chemicals, physical and biological factors, fire and fire protection.

All this documentation also has to be included in an OSH and Environmental Management System and regularly updated.

EXPERIENCES FROM RISK ANALYSIS AND RISK ASSESSMENT

Energy recovery from waste is environmentally better than land filling. Moreover, it is supported by the coming prohibition against land filling. We will probably see the development of not only recovering of energy from combustible waste but also opportunities for a transition to other biomass fuels if those become economically competitive in the future.

This needs efficient methods for risk analysis and risk assessment which have to cover all factors in the field of occupational safety, health, environment and fire protection. Today we have experiences from different methods which probably can, after some research, be combined to one method adapted to the branch.

INCIDENT REPORTING

Management must allocate resources for the administration, information and motivation for incident reporting. The administration and documentation of incidents can be done effectively with a database. Several databases exist today. The branch should recommend one database to be used by all production units so the result can be combined and compared.
The biggest problem normally is to get the employees motivated. This can be overcome by a strong statement from management and 2-4 hours of training and quick feedback from the incident reports to show that immediate action is taken by management.

**OCCUPATIONAL SAFETY AND HEALTH INSPECTIONS**
The most traditional methods to investigate the workplace is through OSH-inspections with or without checklists. There are hundreds of checklists in Sweden. Only around fifty are published by different organisations such as Prevent and others. Today’s inspections are more effective and involve not only the supervisor and the safety representative but also employees. Specific and published checklists for the production of energy from combustible waste and biomass fuel do not exist in Sweden. Here is a possibility for the different companies within the branch to get together and work out methods of risk analysis that can be used by many production units instead of each trying to produce their own.

**GENERAL RISK ANALYSIS WITH A SIMPLIFIED RISK ASSESSMENT**
To get employees involved and to train them to use a simplified risk analysis as well as to make a simplified risk assessment is another very important step to prevent accidents, diseases and fires.

The Joint Industrial Council, (Prevent) has one method called "**Risk thermometer**". The method has a short instruction booklet which describes in three steps with help of three forms and one checklist what to do. The risk assessment has only three levels. The method makes it possible to describe how the work is done and the different risks which exist in each step of the work and the risk level.

The **Risk thermometer** has shown to be very easy to use and can be used for different branches both before the work should start as well as during the work.

I have been introducing the Risk thermometer in all basic training courses for the last five years. Prevent has sold this booklet in more than 4 000 copies.

Prevent has, based on the success of the “Risk thermometer”, developed other booklets such as Ergonomic thermometer, Chemical thermometer, Environmental thermometer, and Workplace thermometer (psychosocial factors).

**THE METHOD “ENERGY ANALYSIS”**
This method, published by The Association of Swedish Engineering Industries, is based on the method to identify where there are different types of energy in a production system. It can be energy caused by electricity, by chemical reaction, by gravity, by movements etc. This method is published as a booklet with some forms and checklists. I have used this method and also introduce this method in different training courses. It has been a very useful method and is easy to use.

**THE METHOD “RIV-RISK INVENTERINGS VERKTYGET” (THE RISK ANALYSIS TOOL)**
This method has been developed for automatic or semi-automatic production. Engineering companies such as SAAB, Volvo and Scania took part in developing the method and are using it regularly.

The method is based on risk analysis and risk assessment in four steps and with 14 different checklists to use if necessary. To be able to use the method requires an experienced leader/supervisor.

I have used the method in one production unit using waste and some other types of factories such as a saw mill, metal workshop etc.
It is necessary to plan and allocate both external and internal resources. The results are often very good and the preventive actions and cost for correction or investment is often paid off within 3-9 months.

THE INTERVIEW METHOD “CRITICAL INCIDENT ANALYSIS, CIA”
All the other methods described previously still have to be complemented with an interview method. This method has its origin from manufacturing of aircrafts in USA. Two external resource persons (consultants with different knowledge, an engineer or a psychosocial expert) interview about 20-30% of all the employees. All categories of occupations should be represented. Each interview is done with one employee in a room. The employee has to describe the different steps in the flow of work/production. He or she will be asked by the interviewer about the worst scenario of risk for accident.

The external resource persons then gather all the information in different areas such as chemical, communication, machineries, building etc.

The risks are described as well as any proposals for improvements that have been mentioned during the interview. The most important step with this method is to send the compiled information back to each work unit and to have them to discuss how relevant the information is, which risk level and how frequently the risk occurs as well as any proposals to prevent the risk on long or short-term bases.

This method can be used in any type of industrial production but also in hospitals. You need to interview at least 15 people to get a good result. It is a good method in a workplace where there can be tensions between the employer and employees.

RISK ANALYSES AND RISK ASSESSMENT USING DIFFERENT KIND OF FUELS
With solid or liquid fuel there are possibilities to identify different chemical and physical parameters and thereby be able to make a risk analysis and risk assessment.

Working with combustible waste or biomass fuel is different. This kind of fuel consists of domestic waste and comparative waste, yard and garden waste, construction waste, demolition waste, waste from reclamation of products, waste specific from one branch, waste not specific for one branch, special waste, inflammable waste and different kinds of biomass fuel.

The risks for accidents, diseases and fires varies with temperature, humidity, different raw materials and chemical components, which can differ depending on the producer of the fuel, etc.

It is necessary that the branch for production of energy from waste and biomass fuel develop a method to evaluate different fuels at the producer’s level so the risks can be considered in all steps of handling the fuel.

SUMMARY
The use of combustible waste and biomass fuel for energy production will continue for many years. The negative effects on the environment, loss of production and materials and on human health in this kind of production can be prevented if the branch gets together to develop a method or methods for risk analysis and risk assessments.

Another effect is that a lot of human suffering caused by accidents, fires, and occupational diseases can be prevented. Furthermore, production units can run with higher profit with less fire and lower cost for insurance.
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TEMPORAL BEHAVIOUR OF MINES AND OBJECTS SIMILAR TO MINES
Stefan Sjökvist and Dan Loyd
Linköping University, SE-581 83 Linköping, Sweden

ABSTRACT
The overall objective of the present mine project is to investigate the possibility of using airborne infrared (IR) sensors for detecting minefield features. In this paper a method is proposed for temporal thermal analysis, based on the extraction of relevant temperature information from diurnal IR images and utilising a combination of thermal modelling and signal and image processing. The paper focuses on the temporal thermal behaviour of relevant objects, e.g., land mines, and how the heat transfer simulations can enhance the possibilities to extract information from airborne collected IR images.

Airborne data were acquired using an IR sensor mounted on an unmanned aerial vehicle (UAV), in this case a helicopter (CAMCOPTER™), from a real field test performed in May 2003 of suspected mine-polluted areas in Croatia. At the same time, a weather station was used in order to provide actual weather data, and a temperature logger recorded a number of temperatures in the soil and in reference markers on the soil.

A numerical model with a set of relevant data, such as geometry, material properties, and surface coefficients is used for predicting the temperatures on the surfaces during the diurnal cycle. The actual weather conditions set the boundary conditions at the surface. The output from the simulations is an estimation of the temperature contrasts between the investigated area and the local background. The predicted contrasts are then compared with the acquired images from the real minefield. The result of the comparison will give essential information for detecting objects and minefields.

The paper also includes some results of temporal thermal behaviour extracted from measurements and analysis of different objects in a real minefield in Croatia. The relevance of the method and possible future development are discussed.
UNDERGROUND DETONATION – THE ENVIRONMENTAL AND SAFE PROCESS

Arild Skirstad
Nammo NAD as, NO-7332 Løkken Verk, Norway

ABSTRACT
Due to its extremely solid rock, the old copper mine in Løkken Verk is most suitable for the purpose of underground detonation of ammunition to be disposed of. Such tests started in 1990, and the discontinued Løkken Verk copper mine company was transformed into the Nammo NAD (Norwegian Ammunition Disposal Company) in the same year.

The first years, Nammo NAD was owned by the Orkla company in Norway. Since 2002, Nammo NAD has been a part of Nammo’s Demil Division. Today the number of employees is 14.

Ammunition is now prepared for detonation at the main level at 810 meters. The main process area (the demolition site) is at the level of around 930 meters. The ammunition is transported down to the level of 810 by an elevator. The demolition sites are parts of the mine’s tunnel system. Air has to be pumped in and out of the mine by ventilation fans; approximately 35 thousand cubic metres an hour. The mine has a natural inflow of about 30 thousand cubic meters of water a year. This water is pumped out in four steps via four sludge separators, and into the Wallenberg mine, which is a closed mine but in use for collecting water from the complete mine system in Løkken Verk. As we deliver water to this system, we have to send in water samples for analysis to the Norwegian environmental department (NIVA).

Nammo NAD is an ISO 9001 certified company. The ISO 14001 standard will be implemented this year. The air and gas outlets from our activity are of no significance, and an outlet concession is not needed according to the Norwegian environmental authorities. Because of the detonations being performed deep down in the mountain, there is no human exposure to noise, fumes, dust, or vibration. All materials (empty boxes, etc.), which have to be moved back to the ground level from the production areas, are inspected and signed for. We have a very good lightning protection system; the work will be stopped if we get an alert for this. Our operators have to qualify through a basic ammunition handling course. This is a tough one, as indicated by the fact that only 50 % of the personnel pass the exam.
SUPERCritical FLUID TECHNOLOGIES
WITHIN CHEMATUR ENGINEERING AB

Lars Stenmark
Chematur Engineering AB, SE-691 27 Karlskoga, Sweden

ABSTRACT
The Chematur Engineering group of companies provides the chemical industry with process plants based on proprietary as well as licensed supercritical-fluid technologies. The range of equipment and applications include supercritical carbon dioxide and supercritical water oxidation (SCWO). The Chematur Engineering demonstration plant for SCWO is described in detail, and results from some treatability studies are given, including the treatment of deinking sludge and sewage sludge. The results clearly show that SCWO is a very effective method for the treatment of sludge.
ABSTRACT

Ammunition, rocket motors, explosives, etc., need frequent investigations regarding safety, present status, and remaining shelf life. Before a decision is made and money is spent on, e.g., expensive modernisation projects, it is of vital importance to get information about the safety of handling objects and the expected remaining shelf life of all ageing sensitive materials and components.

This presentation will describe some typical ammunition and missile objects that are exposed to status and shelf life tests and modern test methods. An ageing-sensitive and potentially unstable part in ammunition is the nitrocellulose propellant charge. Pyrotechnical components like igniters and tracers are the most probable life-limiting components. A typical ageing sensitive component in rocket motors is the solid composite propellant made of CTPB or HTPB, with ammonium perchlorate as oxidiser. During ageing mechanical properties will deteriorate and cause unstable burning with possibly hazardous consequences. Many frequently used materials such as plastics, rubbers, adhesives, etc., tend to be very ageing-sensitive when exposed to explosives.
ADDRESSING ENVIRONMENTAL AND DISPOSAL ISSUES DURING MUNITIONS ACQUISITION

Ian G. Wallace
Cranfield University, Shrivenham, Swindon SN6 8LA, UK

ABSTRACT
Many of the problems of the disposal of munitions at the end of their lives are a consequence of the decisions taken during the acquisition phase. The smart acquisition process, introduced by the UK Ministry of Defence in the past few years, seeks to address some of the disposability and environmental issues at the key decision points early in the acquisition process. The business case for any munition acquisition needs to consider the whole life costs, which include those for disposal as well as examining the implication of ownership on the environment. This paper describes some of the work underway in the UK to develop standards and methodologies to enable environmental and disposability requirements to be specified at the acquisition stage. In particular, it describes the application of Environmental and Safety Compliance Levels (ESCL’s) in munitions acquisition.
"EXCERT", A EUROPEAN PILOT PROJECT FOR DEVELOPING AND MAINTAINING SKILLS AND COMPETENCE FOR PERSONNEL IN THE EXPLOSIVES SECTOR

Hans Wallin 
KCEM AB, SE-691 51 Karlskoga, Sweden

ABSTRACT 
Explosives accidents have claimed the lives of more than a thousand people around the world since the turn of the Millennium. Added to the loss of life has been a significant loss of material values in the form of production resources and capability. Many of the accidents have been caused, not by failure of design, but by human failure. Much of the human failure can be attributed to lack of necessary competence, skills, and training of the people concerned. This paper describes some of the initiatives being taken in Sweden and in the Leonardo da Vinci programme of the European Union to ensure that workers at all levels in the explosives community within the EU have the skills and competence required to safely sustain activities involving explosives. It will describe the development and evolution of a range of explosives competence and the training and qualifications framework being developed to generate and maintain the competence. Finally, the paper will refer to some of the novel training approaches that are being applied in Sweden.
WEAPONS OF MASS DESTRUCTION – A GIGANTIC DISPOSAL CHALLENGE

Kristina Zetterlund
Ministry of Defence, SE-103 33 Stockholm, Sweden

ABSTRACT
When on 11 September 2001 the airplanes flew into the World Trade Center, the world froze. The attack was not only a tragedy of massive proportions in terms of lost lives, but it also signified a threshold in terms of what terrorists were prepared to do in order to achieve their objectives. The anthrax attacks during the autumn of 2001 added to concerns over the gigantic threat posed by weapons of mass destruction (WMD). In addition, WMD proliferation on a state level has come under the world’s spotlights with the war against Iraq and countries like North Korea stealing the headlines. Perhaps less highlighted are dangers such as the world's large number of tactical nuclear weapons and the widespread existence of radiological, chemical, and biological material and know-how. In this presentation, the nature and size of the WMD threat will be discussed as well as potential ways of countering that threat.