

Predicting Graphite/Metals Explosion Severity: from Experimentation to Modelling

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During decommissioning of UNGG (Uranium Natural Graphite Gas) nuclear reactors and wastes reconditioning operations, mixtures of graphite and metal dusts can be encountered. In this perspective, an extensive experimentation has been realized on graphite/magnesium and graphite/iron mixtures to determine their ignition sensitivity and explosivity. The influence of parameters such as the metal content, the ignition energy, the storage humidity, the particle size distribution and the initial turbulence has been considered. It appears that the introduction of such metals can strongly change the behavior of graphite powders: the maximum rate of pressure rise, for example, increases of roughly 355 % comparing to that of simple graphite when adding 30 % wt. of magnesium dust. By means of a vertical explosion tube, an estimation of the laminar burning velocity has been deduced from the apparent flame velocity through the image processing of explosion videos. This experimental study has provided a solid background to better understand these explosion phenomena, to characterize the mixtures behavior by semi-empirical correlations and also to develop and validate a model predicting the severity of a dust cloud in a confined space. Initially conceived for graphite dusts, this model aspires to provide a description of the flame front propagation, leading to the prediction of the explosivity parameters. The dust cloud combustion has been regarded as the combustion of isolated graphite particles, taking into consideration the oxidation kinetic mechanisms and its rate-limiting steps. A finite volume method has been used for the resolution of the transient conservation equations applied to a one-dimension scheme.

1. Introduction

Since prehistory, humans have been characterized by an innate instinct to investigate the root causes of natural events. This thirst for knowledge and will to understand what causes potentially dangerous events allow them to manage the risk, either by preventing them or, if not possible, by limiting their effects. Within this frame of mind, explosions are amongst the phenomena that have been regarded with ever growing interest. At first, the attention was mainly focused on simple gases or dusts, but, in various industries the combustible compounds are seldom encountered in their pure state. The explosive mixtures constituted by several fuels, of which one at least in powdered state, are called "hybrid" and great attention has been paid to them in recent decades. Such mixtures could be encountered in nuclear processes, from the UNGG (Uranium Natural Graphite Gas) reactors dismantling to the recuperation and reconditioning operations of powdered wastes stored in typical equipment such as silos. These mixtures are essentially composed by graphite and magnesium or iron dusts.

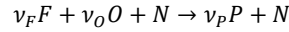
Their fire and explosion hazards are usually quantified in terms of severity indexes: actually, the more energy released during the combustion and the faster it occurs, the greater the destructiveness of the resulting fire/explosion (Lemkovitz, 2014). Considering the impossibility to carry out an all-inclusive experimental study identifying the severity parameters (i.e. mainly the maximum explosion pressure and the maximum rate of pressure rise), the development of predictive models has been of increasing interest, aiming to represent

explosive phenomena and to assess their severity. Saving time, it has the potential of covering a much broader range of explosion scenarios, compared to simple empirical correlations (Skjold, 2007). Within this framework, noteworthy contributions from Kjaldman (1992), Skjold et al. (2005) and Cloney et al. (2014) should be highlighted. Based upon experimental results, this work aims at contributing to this numerical development, by developing and validating a model predicting the severity of graphite/metal clouds in a confined space. It should be underlined that, even if this work focuses mainly on the explosion severity of solid/solid mixtures, the results of tests performed to determine the minimum ignition energy, temperatures or concentration have also been considered to develop this model.

2. Model development

Based on the description of the flame structure, the model aims at simulating a solid/solid mixture explosion, analyzing the resulting temperature, velocity, and concentration fields. In a first step, owing to the complexity of the phenomenon (i.e. the number and the diversity of processes involved), the model has been developed for a dust cloud of isolated graphite particles, which are converted into gaseous products through a static flame. Hence, an Eulerian description of the fluid motion has been used in terms of macroscopic properties: velocity, temperature, mixture density and mass fraction of species.

Four chemical species are supposed to be present in the flow: the solid fuel (F), the oxidant (O) i.e. oxygen, the product (P), and a neutral gas, nitrogen (N). The combustion kinetics is assumed to occur through a one-step irreversible chemical reaction, corresponding to the total graphite oxidation:



where v_F , v_O and v_P are the molar stoichiometric coefficients of the reaction. The detailed oxidation kinetics will be described in paragraph 3.3.

The flow is supposed to be governed by two different types of differential partial equations for mass and energy, and an equation of state. The momentum equation has been neglected, as per assumption of low speeds (e.g. Mach number < 0.2). In this situation the fluids can be considered incompressible, and there is no linkage between the energy, mass and momentum equations (Sivashinsky, 1979). Heat transfer by radiation and flow turbulence have also been neglected in a first approach.

Hence, the one-dimensional model equations read as follows:

- Mass balances (continuity equation and mass conservation for the $N_s - 1$ chemical species):

$$\partial_t \rho + \text{div}(\rho u) = 0 \quad (1)$$

$$\partial_t(\rho y_i) + \text{div}(\rho y_i u) + \text{div}(j_i) = \dot{w}_i \quad (2)$$

where N_s , ρ , u , y_i , j_i , and \dot{w}_i stand respectively for number of species, fluid density, fluid velocity and mass fraction, mass diffusion flux, and reaction rate of species i .

- Mass fraction identity:

$$y_N = 1 - \sum_{i=1}^{N_s-1} y_i \quad (3)$$

- Energy balance:

$$\partial_t(\sum_{i=1}^{N_s} c_{pi} \rho y_i \vartheta) + \text{div}(\sum_{i=1}^{N_s} c_{pi} \rho y_i u \vartheta) + \text{div}(\sum_{i=1}^{N_s} c_{pi} j_i \vartheta) - \text{div}(\lambda \nabla \vartheta) = \dot{w}_\vartheta \quad (4)$$

where c_{pi} , ϑ , λ , and \dot{w}_ϑ stand for the specific heat of species i , the temperature, thermal conductivity, and heat production rate due to the chemical reaction. As a local thermal equilibrium has been supposed (i.e. the time it takes for a fluid particle to adjust to new conditions is short compared with the timescale of the flow), a single equation has been written to calculate the temperature of both gaseous and solid phases.

Four different terms can be identified from the previous differential equations, from left to right: the rate of increase of the fluid element unknown variable, the net flow rate of the variable out of fluid element (convection), the rate of increase of the variable due to diffusion, and the rate of increase of the variable due to reaction.

- Equation of state for the mixture:

$$\rho = 1 / \left(\frac{R}{P_{th}} \sum_{i \in I_g} \frac{y_i}{W_i} + \sum_{i \in I_s} \frac{y_i}{\rho_i} \right) \quad (5)$$

Assuming that the gaseous phase is a perfect mixture of perfect gases: W_i , P_{th} , R , I_s , and I_g are respectively the gaseous mixture molar mass, the thermodynamic pressure, the perfect gases constant, the indices corresponding to the solid species, and to the gaseous ones ($I_s \cup I_g = \{1, \dots, N_s\}$).

The transient conservation equations system has been completed with initial and boundary conditions. Hence, at the inflow boundary the total flux is prescribed while at the outflow boundary the diffusion flux is supposed to vanish. The equations have been implemented in MATLAB® and solved using an explicit finite volume method with a time step of 10^{-4} s. Great attention has been given to the definition of the convection and diffusion fluxes so that the numerical scheme would respect “by construction” the physical bounds satisfied by the variables in the continuous case. For this reason, an upwind scheme has been applied at the faces of the control volumes in the discretization process (Eymard et al., 2000).

This model is able to provide the time and space evolution of the temperature, the pressure and its derivative. Keeping into consideration their maxima values, it can estimate the severity parameters of the dust cloud considered, which are validated by comparison with experimental results.

3. Experimentation as a modelling support

An extensive experimental study has been previously realized to provide the development of the numerical model with a satisfying background. Moreover, it has allowed to justify some of the simplifying assumptions made, as shown below.

3.1. From a turbulent to a pseudo laminar flame velocity, and vice versa

As an Eulerian description of the fluid motion has been used, the flame front can be considered as a fixed location throughout which the unburned reactants are converted into their products. In order to ensure that the flame front does not move, the unburned reactants' velocity should coincide with the opposite of the flame effective velocity. Thus, the laminar propagation velocity of the flame front can be obtained from the flow velocity provided by the resolution of the transient conservation equations system. Consequently, a turbulent flame velocity might be deduced by the means of some relations, such the Schelkin's one (Lewis and Von Elbe, 1985):

$$\frac{S_T}{S_{uL}} = \sqrt{1 + \left(\frac{2u'}{S_{uL}}\right)^2} \quad (6)$$

where S_T , S_{uL} , and u' are the turbulent combustion velocity, the laminar burning velocity, and the velocity fluctuations, respectively. That relation was initially conceived for wrinkled gaseous flames; however, although dealing with a dust, it could give a good estimation of the turbulent flame velocity.

In order to validate the flame velocity values given by the model, experiments have been carried out using a vertical open tube with a 0.07 m-square cross section with two opposite walls made of glass and the others of stainless steel. A Phantom V91 high speed video-camera has been used to record the bottom-up propagation of the flame front in the tube. A mushroom-shaped nozzle was located on the bottom of the tube to disperse the dust homogeneously. Ignition has been realized by means of an electric arc generated between two electrodes placed at 10 cm from the bottom, releasing an energy (from 1 J to 200 J) variable as a function of the discharge time. Records have been analyzed using a model in Simulink developed with the 'Computer vision toolbox' of Matlab (Di Benedetto et al., 2011). The apparent flame front velocity has been corrected by considering the expansion thermic factor representing the density difference between burnt and unburned species. The effect of turbulence has been accounted for by quantifying the flame stretching produced when a perturbation in the flow induces a front deformation. The flow turbulence intensity being strictly linked to the ignition delay t_v (i.e. the time between dust dispersion and its ignition), experiments have been realized at several delays to investigate turbulence impact on the flame propagation. A 'pseudo' laminar velocity resulted as the asymptotic value of the relation between the unstretched flame speed and the ignition delay. This approach, initiated by some authors as Andrews and Bradley (1972), has mainly been applied to gases and its application to dust cloud opens new lines but is still questionable. As a consequence, the term 'pseudo' laminar is used to describe the flame speed obtained by using this method.

For instance, it has been applied to a graphite-magnesium mixture with 30 % wt. of metal (Figure 1). The asymptotic 'pseudo-laminar' flame front velocity reaches approximately $0.18 \text{ m}\cdot\text{s}^{-1}$, which is globally consistent with unstretched laminar burning velocities obtained by other authors, such as Dahoe (2000) for starch powder, i.e. between 0.15 and $0.3 \text{ m}\cdot\text{s}^{-1}$. As no literature data are available for graphite/metals mixtures, the previous method has also been tested successfully on wheat starch.

These experiments have also allowed to validate the hypothesis of 'low speeds': actually, a value of the Mach number of $2 \cdot 10^{-3}$ (and so, lower than 0.2) has been obtained, confirming the possibility to neglect the momentum equation in the mathematical resolution of the model.

The maximum values of the severity parameters in turbulent conditions have also been obtained, allowing to calculate the deflagration index (K_{St}) as function of the turbulence level determined by particle image velocimetry (PIV) and using equation (6) to transform the 'pseudo' laminar velocity into S_t at a given u' and equation (7) (Dahoe, 2000):

$$\left(\frac{dP}{dt}\right)_{max} = \frac{3(P_{max} - P_0)}{R_{vessel}} \left(\frac{P}{P_0}\right)^{\frac{1}{\gamma}} \left[1 - \left(\frac{P_0}{P}\right)^{\frac{1}{\gamma}} \frac{P_{max} - P}{P_{max} - P_0}\right]^{\frac{2}{3}} S_T \quad (7)$$

For instance, by considering the mixture at 30 % wt. of magnesium with a dust concentration of 750 g.m^{-3} , an ignition delay of 30 ms, a 'pseudo' laminar velocity and γ values respectively of 0.53 m.s^{-1} (Figure 1) and 1.41, a deflagration index of 26 bar.m.s^{-1} has been obtained. This is consistent with the results obtained in the 20 L explosion sphere: in the same conditions, experiments have returned a K_{St} of 20 bar.m.s^{-1} . It should be noted that a turbulent level of 0.2 m.s^{-1} has been used for the calculation, which is lower than the value required for the standard experimental evaluation of K_{St} (NFPA68, 2002).

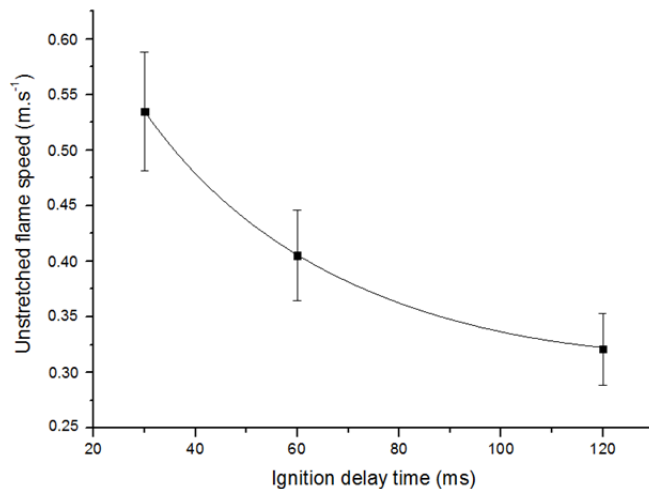


Figure 1: Unstretched flame speed evolution as a function of ignition delay for 30 % wt. Mg/C mixture. Powder concentration = 750 g.m^{-3} , ignition energy = 100 J.

3.2. Oxidation kinetics for graphite and metals particles

Graphite combustion actually appears as a step-process in which some intermediary species (such as H, O, OH) transform into others (e.g. HO_2 , H_2O , CO, CO_2) until the formation of the expected gaseous products occurs (Otón-Martínez et al., 2013). In order to limit its complexity, the model makes the assumption that the combustion kinetics occurs through a one-step irreversible chemical reaction, corresponding to the total graphite oxidation. An experimental study realized in the 20 L explosion sphere, both on simple dusts and hybrid mixtures, suggested that this simplifying assumption can be regarded as reasonable and be preserved when the model will be extended to hybrid mixtures. Indeed, by considering the pressure history and its derivative recorded in the test vessel for simple graphite dust (the continuous line in Figure 2), a single peak corresponding to the graphite combustion has been observed indeed. It is worth noting that the first peak in the graph on the right-hand side of Figure 2 refers to the chemical igniters contribution and is not linked to the combustion. A similar situation has been found for hybrid mixtures of graphite and magnesium up to 30 % wt. of metal for which the presence of a single explosion stage has been registered; hence, the two solids react at the same time scale like a single fuel. This assertion has been confirmed considering combustion time values: 31 ms for pure magnesium and 95 ms for graphite dusts, whereas a 30 % wt. Mg/C mixture is characterized by a combustion time approximately 25 % lower than the one of pure carbon.

Although magnesium dust rapidly vaporizes to react in homogeneous gas phase (Yetter et al., 2009), which turns the original hybrid solid-solid mixture into a hybrid gas-solid one, it has not been possible to observe the peculiar behavior found by Denkevits (2007) for classical hybrid gas-solid mixtures constituted by hydrogen and graphite. In that case, fuels contributions appeared clearly separated and there were several phases of combustion: the solid fuel combustion occurred only after the gas explosion which provided the necessary triggering energy.

Similar considerations have been made for hybrid mixtures of iron and graphite dusts: they are characterized by a single 'apparent explosion stage' as well.

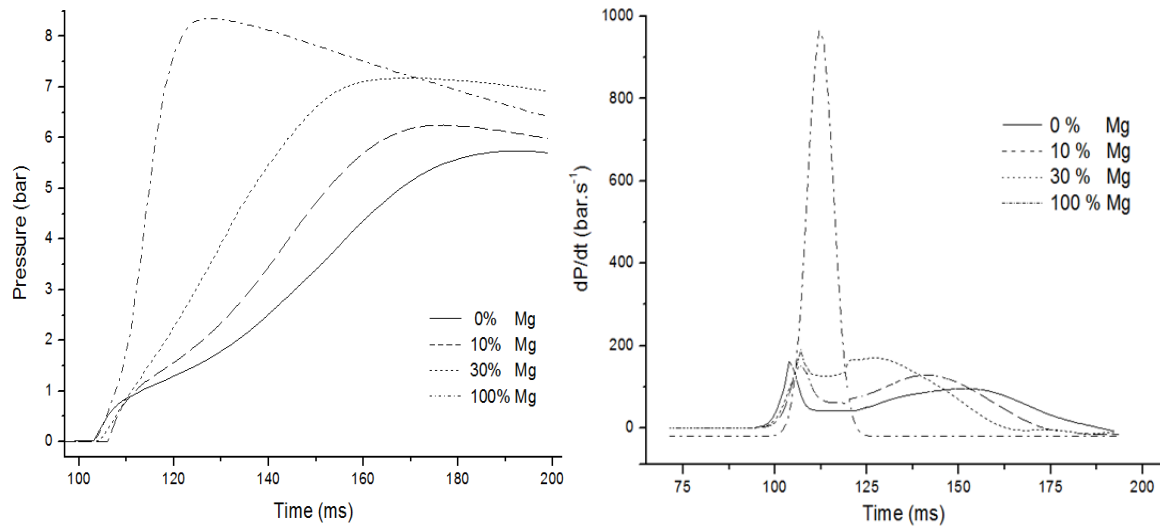


Figure 2: Explosion pressure time evolution (left) and rate of pressure rise (right) at different magnesium weight percentages. Dust concentration = 500 g.m^{-3} , ignition energy = 10 kJ , $t_v = 60 \text{ ms}$.

Then, it appears that, if the graphite combustion involves in practice different steps, its kinetics still can be modelled by only considering its most limiting step. A shrinking core model without ashes generation has been retained to describe the evolving particle size during the oxidation. The heterogeneous reaction occurs at graphite particles surface and the reaction limiting-step is the oxygen diffusion throughout the gaseous layer that surrounds the particles. Once reached the surface, the reaction occurs with the following rate expression (Levenspiel, 1999):

$$\dot{w}_F = A e^{\left(\frac{-E}{R\theta}\right)} C_{O_2}^n (1-x)^{\frac{2}{3}} \quad (8)$$

where A , E , C_{O_2} , n , and x stand for pre-exponential factor and activation energy for the Arrhenius-type expression for chemical rate, oxygen concentration, reaction order referring to oxygen, and reaction conversion degree. This assertion has also been verified by characterizing the ignition sensitivity of these dusts. Graphite and magnesium powders have not been ignited during minimum ignition temperature tests carried out on dust layers, up to $400 \text{ }^\circ\text{C}$. However, the introduction of metals powders can strongly changes the behavior of a graphite cloud, when the oxygen accessibility is improved: the minimal ignition temperature decreases of about $300 \text{ }^\circ\text{C}$ when adding only $5 \text{ } \%$ wt. of magnesium dust.

3.3. Thermal transfer in a graphite/metal cloud

Thermal radiation has been neglected in the energy conservation equation. Although it plays a dominant role in energy transport within dust flame, as shown by Ogle et al. (1984), especially at high temperatures such as those achieved in the flame front, one could estimate that the error induced by this assumption is still acceptable in the first-phase development of the severity model, considering graphite dust's characteristics.



Figure 3: Flame radiation for $30 \text{ } \%$ wt. Mg/C mixture (left) and for pure lycopodium powder (right) by way of comparison. Dust concentration = 750 g.m^{-3} , Ignition energy = 100 J , $t_v = 60 \text{ ms}$.

Actually, graphite acts very similarly to a black body (i.e. an opaque and non-reflective body) and its radiation might be considered as isotropic, i.e. the magnitude of the intensity is equal in all directions. On the contrary, radiant thermal energy due to reflection is more marked in presence of metals and their oxides as confirmed by experiments carried out using the flame propagation tube (Figure 3). The greater the metal amount, the

thicker is the flame thickness. As a consequence, this type of heat transfer will not be neglected in a further step when the model will be extended to hybrid mixtures constituted by graphite and metals. Particles internal heat transfer times have also been considered: $6.5 \cdot 10^{-2}$, $1.1 \cdot 10^{-3}$ and $8.2 \cdot 10^{-5}$ ms for graphite, magnesium and iron, respectively. Comparing these values with the typical particle combustion times, one may observe that the solid phase reaches the gaseous phase temperature in a negligible time compared to the reaction one. The particles heating occurring very rapidly, the assumption of local thermal equilibrium made during the conception of the model is verified.

4. Conclusions

A mathematical model is presented to simulate severity of graphite dust explosions, supported by an extensive experimental study. The resulting temperature, pressure, velocity, and concentration fields are analyzed to gather information about severity parameters and pseudo laminar flame propagation speed, from which a turbulent one could also be deduced. In a further step, the model will be extended to solid/solid mixtures, especially taking into account the magnesium vapor-phase burning and the enhancement of the thermal transfer by radiation or the oxygen diffusion limiting step, though its oxide layer. The influence of the particles size distribution could also be considered, the thermal transfers being strongly dependent on this parameter.

References

- Andrews G.E., Bradley D., 1972. Determination of burning velocities: A critical review. *Combustion and Flame* 18, 133–153.
- Cloney C.T., Amyotte P.R., Khan F.I., Ripley R.C., 2014, Development of an organizational framework for studying dust explosion phenomena, *Journal of Loss Prevention in Chemical Industries* 30, 228-235.
- Dahoe A.E., 2000, Dust explosion: a study of flame propagation, PhD thesis. Delft University of Technology, Delft, the Netherlands.
- Denkevits A., 2007, Explosibility of hydrogen-graphite dust hybrid mixtures, *Journal of Loss Prevention in the Process Industries* 20, 698-707.
- Di Benedetto A., Garcia-Agreda A., Dufaud O., Khalili I., Sanchirico R., Cuervo N., Perrin L., Russo P., 2011, Flame propagation of dust and gas-air mixtures in a tube, *Proceedings of the 7th Mediterranean Combustion Symposium*, Chia Laguna, Cagliari, Sardinia, Italy.
- Eymard R., Gallouët T., Herbin R., 2000, *Finite Volume Methods*, Handbook for Numerical Analysis, Ph. Ciarlet J.L. Lions editors, North Holland.
- Kuai N., Li J., Chen Z., Huang W., Yuan J., Xu W., 2011, Experiment-based investigations of magnesium dust explosion characteristics, *Journal of Loss Prevention in the Process Industries* 24, 302-313.
- Kjåldman L., 1992, Numerical flow simulation of dust deflagrations, *Powder Technology* 71, 163-169.
- Lemkovitz S.M. and Pasman H.J., 2014, A review of the fire and explosion hazards of particulates, *Powder and Particle Journal* 31, 53-81.
- Levenspiel O. (1999). *Chemical Reaction Engineering*. Third Edition. John Wiley & Sons.
- Lewis and Von Elbe, 1985, *Combustion, flames and explosions of gases*, 3rd edition Academic Press.
- NFPA 68 (2002). *Guide for venting of deflagrations*, Quincy, Massachusetts: National Fire Protection Association.
- Ogle R.A., Beddow J.K., Vetter A.F., Chen L.D., 1984, A thermal theory of laminar premixed dust flame propagation, *Combustion and Flame* 58, 77-79.
- Ogle R.A., Beddow J.K., Chen L.D., Butler P.B., 1988, An investigation of aluminum dust explosions, *Combustion Science and Technology* 61, 75–99.
- Otón-Martínez R.A., Velasco F.J.S., García-Cascales J.R., Vera- García F., 2013, Modelling of dust mobilisation and explosion. Experimental validation, Technical Report, Universidad Politécnica de Cartagena.
- Russo P. and Di Benedetto A., 2007, The effect of turbulence on the theoretical evaluation of dust explosions severity, *Chemical Engineering Transactions* 11, 983-988.
- Sivashinsky G.I., 1979, Hydrodynamic theory of flame propagation in an enclosed volume, *Acta Astronautica* 6, 631-645.
- Skjold T., Arntzen B.J., Hansen O.R., Taraldset O.J., Storvik I.E., Eckhoff R.K., 2005, Simulating dust explosions with the first version of DESC, *Process Safety and Environmental Protection* 83, 151-160.
- Skjold T., 2007, Review of the DESC project, *Journal of Loss Prevention in the Process Industries* 20, 291-302.
- Yetter A.R., Risha G.A., Son S.F., 2009, Metal particle combustion and nanotechnology, *Proceedings of the Combustion Institute* 32, 1819-1838.