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Graphite Dust Deflagration

A Review of International Data with Particular Reference to the Decommissioning of Graphite Moderated Reactors

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REPORT SUMMARY

The graphite moderators of retired gas-cooled nuclear reactors present a difficult challenge during demolition activities. As part of the EPRI graphite initiative on the technical issues involved in the management and disposal of irradiated nuclear graphite, this report examines the international data on dust deflagration relevant to the decommissioning of graphite-moderated reactors. The report concludes that the risk of an explosion involving graphite dust during decommissioning is extremely low, and should not cause concern in planning a decommissioning strategy. Several international organizations, including EdF CIDEN (France), SoGIN (Italy), UKAEA (UK) and NUPEC (Japan), collaborated in this program by providing data.

Background

A previous EPRI report (1013091), *Options for Graphite Treatment, Recycling, or Disposal,* included an Appendix entitled "Assessing the Potential Risks in Decommissioning from Carbonaceous Dusts" which briefly reviewed the then presently-available information in the context of the decommissioning of graphite-moderated nuclear plants. It concluded that the risks of a graphite- or carbonaceous-dust explosion during decommissioning activities are in almost all circumstances extremely low. However, concern about the initiation and effects of any explosive event in a reactor during operation or decommissioning led to a request for a more detailed evaluation. Any mechanical damage from the resulting pressure pulse is potentially capable of breaching the containment and permitting the dispersal of radioactive materials into the environment, in addition to the more direct risks to nearby personnel. In the decommissioning scenario, the 'containment' is more likely of a temporary nature, and hence more vulnerable.

Objectives

To collate all of the international dust deflagration work.

To determine the conditions under which graphite can be safely handled in decommissioning without potentially causing dust deflagration events.

Approach

At the start of this project it was becoming clear amongst a number of European EPRI members that a more comprehensive treatment of dust issues would be required to support arguments to safety bodies for decommissioning activities in graphite-moderated reactors. France's "graphite decommissioning" team initially discussed a collaboration between the UK (UKAEA Southern Division), France (EdF CIDEN) and Italy (SoGIN). They planned to issue a pan-European document combining their experimental experiences. EPRI's involvement has now extended the collaboration to include contributions from NUPEC in Japan (on behalf of the Japan Atomic Power Co.)

The project team collated the data from all of the organizations and described basic dust-explosivity assessment techniques. The report includes arguments for the rejection of the term "explosion" in favor of "deflagration" based upon improved understanding of the mechanism of flame propagation through suspended combustible materials. It also includes a discussion of the relevant work conducted in each country in full detail, demonstrating how each piece of work complements the others

Results

There is good agreement between the results of the various international programs on this topic. Graphite dust is only weakly explosive. A minimum energy of 2,000 Joules is required to bring about any deflagration and even that has a low deflagration index. Only the smallest particles participate in deflagration, and these are likely to agglomerate with time or be removed in any practical decommissioning scenario. During decommissioning it is easy to remove by design at least one of the conditions, all of which must be simultaneously satisfied for deflagration to occur. Experience with decommissioning of WAGR in air in the UK has been good, and supports the above conclusions.

The report therefore concludes that the risk of a dust explosion involving graphite dust during reactor decommissioning is extremely low, and should not cause particular concern in planning a decommissioning strategy. In the course of designing the strategy, however, it is prudent to eliminate any potential risk by eliminating one or more of the essential conditions for deflagration that are identified in the report

EPRI Perspective

The EPRI graphite initiative started in 2005, with a review of available data (EPRI Report 1013091), which led to further work on three specific technical areas. The work described in this report provides an international consensus on the dust explosion issue. Organizations can use it where appropriate to justify and underpin the safe dismantling of graphite reactors in air. The report defines precautions necessary to avoid safety hazards. The next graphite project, which is in progress, reviews the existing data on the leaching of radioisotopes from graphite moderators, including their relevance to the dismantling of graphite structures. Another project is currently investigating graphite radioisotope separation technology, as there is a widespread view that disposal would be greatly facilitated if carbon-14 could be removed from the graphite blocks. This project involves an engineering feasibility study of the most promising techniques for C-14 isotope separation.

Keywords

Low level waste disposal
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INTRODUCTION

In a recent review of the “Options for Graphite Treatment, Recycling, or Disposal…” in the context of the decommissioning of graphite-moderated nuclear plant[1] [1], the present authors included an Appendix entitled “Assessing the Potential Risks in Decommissioning from Carbonaceous Dusts” in which the then presently-available information on this subject was briefly reviewed, forming the conclusion that the risks of a graphite- or carbonaceous-dust explosion during decommissioning activities are in almost all circumstances extremely low, in contrast to the apparent perceptions of nuclear regulators and safety officials who have come to regard not only graphite dust but even bulky graphite components as ‘hazardous’ material.

The concern about the initiation and effects of any explosive event in a reactor during operation or decommissioning is understandable. Any mechanical damage from the resulting pressure pulse is potentially capable of breaching the containment and permitting the dispersal of radioactive materials into the environment, in addition to the more direct risks to nearby personnel. In the decommissioning scenario, the ‘containment’ is more likely to be of a temporary nature, and hence more vulnerable.

Conversely, one does not wish to be driven unnecessarily to make costly and unnecessary provision for the possibility of a dust explosion during decommissioning if the true risk of such an event is miniscule.

Whilst the comprehensive treatment of the mechanism of graphite oxidation in air given in [1] hopefully allays much of this fear for both dust and bulk material, it was at the same time becoming clear amongst a number of European EPRI members that a more comprehensive treatment of the dust issues would be required to support arguments to safety bodies for decommissioning activities in graphite-moderated reactors. A collaboration between the UK (UKAEA Southern Division), France (EdF CIDEN) and Italy (SoGIN) was initially sought by EdF, with a plan to issue a pan-European document combining their experimental experiences: this has now been extended through EPRI to include contributions from NUPEC in Japan (on behalf of the Japan Atomic Power Co.).

A description of basic dust-explosivity assessment techniques is given first, together with the arguments for the rejection of the term “explosion” in favor of “deflagration” based upon the improved understanding of the mechanism of flame propagation through suspended combustible materials.

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[1] Or any nuclear plant containing graphite components such as fuel sleeves, reflector blocks, etc.

The relevant work conducted in each participating country is discussed in full detail, demonstrating how each piece of work is complementary to the others and that their combined findings strongly reinforce the conclusion that the explosion risk from graphitic dusts in operational reactor situations and in decommissioning is extremely low. It is further concluded that additional work in support of this issue is unnecessary.

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THE NATURE OF SOLID GRAPHITE, AND GRAPHITE OR CARBONACEOUS DUSTS, IN REACTOR SYSTEMS

The perceived “problem” of graphite and carbon dust “explosivity” in reactor systems stems from two widely-held preconceptions:

1. that graphite itself is a dangerously combustible material, largely based on the “evidence” of two significant graphite “fires” in reactors at Windscale (UK) and Chernobyl (Ukraine); and
2. that suspensions of finely divided carbonaceous material in air or other oxidizing atmospheres are potentially capable of allowing a flame front to propagate, with the consequent creation of a pressure pulse and possible local disruption as a result.

The first of these issues was comprehensively discussed in [1], where it was demonstrated that direct “burning” of nuclear-grades graphites does not occur, and that the mechanism of oxidation in air, although complex and moving through a number of different regimes controlled respectively by chemical rate, gas diffusion, and mass transport as the temperature rises, is extremely well understood. Highly-purified forms of graphite in bulk are in fact extremely difficult to oxidize quickly, having an extremely low vapor pressure unless the temperature is well in excess of 3000ºC (which eliminates any possibility of flame formation). Graphite is an extremely efficient black-body radiator which means that it loses heat very readily, although the thermal conductivity is somewhat diminished by neutron damage when irradiated. The specific heat capacity is quite high.

Its use as a ceramic in furnace linings, as electrodes in high-temperature processes such as aluminium smelting and in arc lamps, and in other situations where a high-performance heat-resistant material is required, further demonstrates that it is implausible to consider it a fire hazard – indeed, in the form of Graphex® powder, it has been utilized extensively as a fire extinguishant.

Ref [1] went on to consider the two major incidents at Windscale and Chernobyl in detail, assessing the latest-available evidence from each. In both cases there is no dispute that graphite was heated to extremely high temperatures, and that the oxidation which occurred in the available air supply at such temperatures was exothermic and thus adding heat to the system. However, in neither case was graphite oxidation the cause of the incident, this being attributed to a fuel and/or isotope-cartridge fire initiated by Wigner-energy release in the Windscale accident, and to an uncontrollable reactor-physics excursion in the Chernobyl case. When blocks of graphite were ejected from the Chernobyl core they were certainly hot enough to start fires in other materials such as asphalt roofing sheets, but the red-hot blocks were observed to cool immediately upon ejection despite the presence of a free supply of air.

This behavior of nuclear-grade graphite is in contrast to that of lower-grade carbonaceous materials; a coal fire is demonstrably self-sustaining, and this is possible because of at least three features which do not apply to nuclear-grade graphite blocks: (i) the presence of more reactive non-graphitic carbon; (ii) the presence of volatile materials; and (iii) the presence of impurity materials which are catalytic, such as compounds of transition metals. Such a coal fire remains self sustaining until the non-combustible (ash) content of the residual solid material rises to a point at which its radiative losses and heat-sink capabilities outweigh the heat input from the oxidation of the remaining carbonaceous materials, whereupon the fire dies.

Thus, our starting point in the present review is that bulk nuclear-grade graphite components cannot burn: they oxidize slowly in a controlled fashion if sufficiently heated in air or an oxidizing atmosphere, but are by definition non-flammable and do not present any form of fire hazard either in-reactor or during external handling.

The second issue, concerning the behavior of finely-divided dust suspensions is, at first encounter, a much more realistic potential “threat”. The whole science of dust oxidation behavior originated from a history of explosions in coal mines, and the early account of the recognition of the problem, documented in [2], makes interesting background reading. Here again, it is the volatiles content of the dust which presents the principle reason for the hazard when there is insufficient inert material present to ‘dampen down’ the flame propagation (a process we shall discuss in detail later)[2]. Many serious accidents have also occurred in flour mills and in related food-industry environments handling such materials as powdered starch, skimmed-milk powder, etc. The resulting explosions have had the power to demolish multi-story buildings and to cause numerous fatalities, especially where no thought had been given to seeking to eliminate the principal cause of such events – ignition sources – or to the provision of systems for explosion-pressure relief. Indeed, the principles of today’s safety engineering for such plants were largely learned from bitter experience.

Field [3] documents much of this experience in what for many years has been one of the principal text books on this subject, and it is most useful for defining the criteria which must be simultaneously satisfied if a dust explosion is to result:

> the dust must be combustible (the presence of volatile constituents is important here);
>
> the dust must be airborne, implying either a turbulent gas flow or some physical disturbance which allows the dust to fall freely through the gas atmosphere;
>
> the atmosphere must support combustion;
>
> the particle size must be optimized for flame propagation;
>
> the dust concentration must fall within the exposable range; and
>
> an ignition source of sufficient energy to initiate flame propagation must be in contact with the dust suspension.

---

[2] Of course, in the mining situation, flammable gases such as methane may also contribute.

If a disruptive explosion is to result, there is an additional condition:

the dust must be in a confined space which inhibits the relief of the pressure pulse arising from the ignition of the dust.

In assessing the overall risk, secondary effects must be borne in mind. A pressure pulse arising from the ignition of a small amount of dust generated in a cutting operation could cause dusts elsewhere in the system to be levitated and then themselves contribute to a secondary explosion.

We thus see that the science and engineering issues underlying the possibility of a dust explosion are quite complex and are deserving of careful study and analysis in order to present comprehensive safety arguments to regulatory and safety officials. The possibility of eliminating one of the above-mentioned criteria may seem to be a simple solution for avoiding the problem, and to some extent this is so. However, sufficient data and experience now exist to enable a far more comprehensive assessment of the issue, and it is the purpose of this review to provide that assessment.

There are two principal sources of graphitic or carbonaceous dusts in reactor circuits. The first of these, clearly, is the moderator and reflector graphite blocks themselves.

During construction of the reactor graphite stack, some dust generation is inevitable. However, in most cases, provision for removing this was made at the time using vacuuming. During operation some movement of block against block is inevitable, leading to the possible generation of dusts of rather unpredictable particle size. For example, the stabilizers of the fuel loading machines have left shallow marks in the fuel-channel wall graphite of the French Saint-Laurent reactors. Some reactors experienced particular events which could lead to dust generation: for example, in the Windscale prototype AGR in the UK, a significant problem occurred initially with vibration of control rods. Erosion by rapid gas flows has also been suggested as a means of dust generation.

Such dusts as do form may then be moved around the gas circuit, collecting in regions where the influence of the flowing coolant is at a minimum. There are at least six distinctive deposition mechanisms which are worthy of consideration when assessing where dusts might be found within the reactor. There are:

gravitational deposition;

inertial deposition;

streamline interception deposition;

diffusional deposition;

thermal deposition; and

electrostatic deposition.

Of these, thermal deposition due to thermophoretic forces is probably the least significant. Gravitational deposition is essentially self-explanatory, and always present whatever the flow conditions: the settling rate increases with particle mass. Inertial deposition occurs when a streamline carrying a particle is stopped or abruptly deflected by a surface or obstacle, whereupon the inertia or momentum of the particle carries it to the surface where it is retained. This principle was employed in the UK in the so-called ‘central inertial collectors’ initially employed in selected channels of advanced gas-cooled reactors to remove oxide particles and other circuit debris. It is applicable to dust sizes in excess of about 1μm. Below this size, and particularly in particles less than around 0.3μm, deposition occurs by diffusive mass transfer. This difference arises because dusts in this size range experience Brownian movement by molecular bombardment and tend not to follow the fluid streamlines. A concentration gradient is established across a boundary layer of fluid adjacent to the surface across which the particles diffuse. Streamline interception deposition occurs if the particles pass within one particle radius of a surface, since they then make contact with the surface and will be retained. Finally, electrostatic deposition requires the presence of an electrical charge on the surface, something which is unlikely for a graphite surface since it is electrically conducting.

If collected dusts remain in the heated or irradiated part of the circuit for any length of time, then they will themselves be subject to oxidation either thermally (in air-cooled reactor systems) or through radiolytic oxidation (air- or CO_2-cooled systems). In HTR designs, oxidation is a low probability event dependent upon the introduction of impurities into the helium coolant either through a fault condition or through incomplete purging after reactor maintenance activities. The oxidation will serve to reduce particle size initially, and may increase porosity.

Where dusts (or the original blocks) are irradiated at rather low temperatures (<250ºC), stored “Wigner” energy may accumulate within the graphite, changing its heat capacity and exothermicity upon oxidation.

Such dusts will also become contaminated with other types of circuit dusts. These are most likely steel-oxidation products (metal oxides), which may variously be considered either as catalysts or inert material, an issue which is explored further in the work reported here. With time the particles may agglomerate.

A second source of graphitic dusts arises after the completion of reactor operation, in activities associated with decommissioning. Such dusts are likely to be generated locally through adjacent cutting operations, or during the removal of components. These freshly-formed dusts are likely to have properties much more akin to the originating graphite – for example, a much lower concentration of impurities than general circuit dusts, unless cutting operations themselves produce particulate material which needs to be taken into consideration.

Not all carbonaceous dusts found in reactor circuits will necessarily be graphitic. In CO_2-cooled reactor systems there is a history of carbonaceous deposition on fuel elements, on boiler tubes, and on graphite components themselves arising from the radiolytic decomposition of CO in the coolant (this is a corrosion product from radiolytic oxidation of graphite) or from minor organic impurities (especially where methane has been added as an oxidation inhibitor). There is a strong dependency between the extent of formation of such carbonaceous deposits and the impurity hydrogen content of the coolant: a higher hydrogen content reduces the propensity to this deposition. Graphite-monitoring programmes in the UK, described in [4], have found a wide variation in such deposit concentrations on graphite up to 30,000 ppm (3% by weight of underlying graphite) in some Magnox cores, with related non-graphitic carbon deposits found of the boiler tubes in steam-raising units of both Magnox and AGR systems. In severe cases arising from unusual coolant compositions (e.g. the Japanese reactor Tokai 1 in the early 1980s) the deposits have also disrupted heat transfer from Magnox fuel elements.

Carbonaceous deposition on AGR fuel elements has been found to be more persistent, and additionally related to the ppb concentrations of impurity gases such as H_2S[3] which can affect the chemistry of surfaces on which deposition might occur. A related 'carbon-transport' is also possible in HTR systems, moving carbon atoms from the graphite fuel assemblies to other parts of the gas circuit.

Such deposited materials are less likely to be mobile than graphitic dusts, but if they are present they are likely to be much more finely divided and, as non-graphitic, potentially more reactive – up to 100× more so than the underlying graphite [4]. Thus, in our present review, note needs to be taken of the possibility of the presence of these materials.

It should also be borne in mind that only dusts which can be resuspended are of importance in assessing the potential for deflagration. In preparing a safety case for a decommissioning programme, careful thought needs to be paid to what potential incidents could result in this, and some may not be immediately obvious. As an example, it may be noted that, in the UK WAGR safety case, the accidental dropping of a large steel plate on to a surface covered in static dust was found to be one of the major risks, as was a primary propane explosion caused by failures of the hoses supplying gas torches used for flame cutting of metal structures.

Layers of deposited dust can however present a separate hazard if they become heated, such as smouldering and possible self-ignition, and this should be borne in mind in the preparation of decommissioning safety cases.

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[3] The principal sources of sulphur are gas-circulator-bearing oil and impure shield-wall carbon.

3
GENERAL PRINCIPLES OF DUST DEFLAGRATION

3.1. The Process

3.1.1. Definitions

An "explosion" is the very rapid release of energy from an exothermic reaction which rapidly raises the temperature and pressure of the oxidizing medium and gaseous products. A dust "explosion" can potentially occur when finely divided combustible material is dispersed in an atmosphere containing enough oxygen to support combustion and where an ignition source of sufficient energy to initiate combustion is present. In exceptional circumstances – *i.e.* with magnesium dust – explosion in other gases such as nitrogen would be possible, but this is not relevant for carbonaceous materials. In the extreme case of evidence of contamination of graphite stacks with magnesium from fuel cladding, then special considerations are clearly necessary. Although other gases such as nitrous oxide are also capable of supporting combustion of carbons to some extent, they are considered to be irrelevant here.

It is perhaps necessary to define "*dust*". An old British Standard [5] defines a "powder" as being composed of discrete particles of dry material having a maximum dimension of less than 1000 μm; a "grit" is defined as hard particles, usually mineral, natural or industrial in origin which are retained on a 75 μm British Standards test sieve; whilst a "dust" is said to be particulate matter which has been airborne and which passes through a 75 μm sieve. In terms of dust explosions, this definition is not fully appropriate since particulate matter in excess of 75 μm is known to be capable of causing explosions. Ref [3] recommends that in the current context, "*dust*" should be regarded as "*combustible particulate matter capable of being airborne and having a particle size less than 500* μ*m*". However, as will be seen later, the ISO standard test limits 'eligible' dust to a maximum particle size of 63 μm.

It is also important to differentiate the terms "explosible" and "explosive", the latter generally applying to something which can explode in its own right (with a self-contained oxidizing agent), whereas "explosible" means that the material can undergo an explosion only if presented with appropriate conditions which include an oxidant. Thus, maize flour, a common 'standard' material in dust-explosion research, is explosible but in no context could be considered to be an explosive

If a dust suspension is "explosible" it means that a flame front can propagate through it. This phenomenon is discussed in more detail in Appendix A. Usually this will be at significantly less than the speed of sound, in contrast to a gas explosion. Thus, the event will not usually be a *detonation*, in which the flame front and the compression wave proceed together, representing a sonic "bang" which for some solid or liquid explosives can reach a shock-wave speed of 1500 –

9000 m.s^{-1}, but rather a *deflagration*, with a sub-sonic propagation of the flame front lagging behind the compression wave and which has been conveniently described as "more of a '*whoosh*' than a '*bang*'". Detonation in generally produces a higher overpressure than a deflagration. These terms are defined rather more precisely in [6] in terms of solid and liquid materials, and the transition between detonation and deflagration is explored in more detail than is required here. Dust explosions which initially produce flammable gaseous oxidation products from the powder which can themselves ignite and contribute to the propagation of the flame front may result in 'borderline' cases in which dust explosions do approach a detonation[4]. This possibility is also facilitated by powerful ignition sources and high turbulence. Ref [6] also offers useful up-to-date background on the thermochemistry, thermodynamics and kinetics of explosion processes.

We therefore prefer to use the term *deflagration* in this review to describe the process of flame propagation through a suspended combustible dust.

Despite this lack of a supersonic propagation of the flame front, high pressures can be generated as a result of the sudden combustion of solid particles to gaseous products. Indeed, a dust deflagration can be much more violent than a gas explosion because of the conversion of larger masses of solid material into gaseous products. As previously mentioned, not only is the absolute pressure generated in the reaction important, but possibly more so is the rate of pressure rise, since this conveys a potentially more destructive impulsive loading to the surrounding structures. Thus, the maximum rate of pressure rise is a very important parameter in defining the outcome of a particular deflagration, leading to a definition of the *deflagration index* K_{st}:

$$K_{st} = \left(\frac{dP}{dt}\right)_{\max} . \; V^{\frac{1}{3}}$$

V represents the immediate volume surrounding the deflagration, *e.g.* the standard test apparatus, and serves to normalize the deflagration index to a common basis with units bar.m.s^{-1}. The subscript '*st*' derives from the German word for dust – 'staub' – and is used to distinguish the parameter from the equivalent one for a gas explosion.

This expression derives partly from the work of Bartknecht [7] who made studies in vessels of a large range of sizes (up to 60 m^3) and observed that, for constant dust concentration, pressure and ignition characteristics, the maximum explosion pressure achieved remained essentially constant in all of his vessels whereas the maximum rate of pressure rise varied with volume as in the above expression.

The deflagration characteristics of highly-reactive dusts are found to be essentially independent of ignition energy, whereas for low-reactive dusts (and graphite falls into this category as will be seen), both the maximum pressure attained and particularly K_{st} are strongly dependent on ignition energy [8]. K_{st} may be regarded as a measure of the flame-front rate of reaction, and is directly related to the flame-front burning velocity.

---

[4] Aluminum powder is a special case which produces a detonation despite the formation of no gaseous products.

A similar expression may be derived for flammable gases, based upon initially quiescent gas/air mixtures. Here the term is given as K_g, and it is found to exhibit a dependency upon the volume of the vessel employed. This is relevant in the present review since a flammable-gas driver was employed in the UK work discussed in Section 4.4.

The earliest known account of a dust deflagration comes from an eighteenth-century flour mill in Turin [9]. At the time, it was thought that the flour must have produced a flammable gas which then ignited. Explosions in coal mines at the same period were likewise always attributed to flammable gas, and it took nearly 100 years before it was realized that it was the dusts themselves which were frequently the cause of the incidents. With the increasing industrialization at the end of the nineteenth century and the beginning of the twentieth, a wider variety of materials were becoming involved in dust incidents, with serious incidents involving loss of life in a Scottish mill, a French dye factory and an American starch factory all promoting research into the process. In one year alone (1907) there were 1148 deaths in the US coal-mining industry, many attributed to the effects of the ignition of suspended coal dust, and this led to the establishment of the US Bureau of Mines which was to contribute over 60 years of research into the problem in a wide range of materials in addition to coal.

Ref [3] charts the history of many of the more serious explosions which have occurred, analyses them in detail, and discusses the establishment of research bureaus in a number of other countries. The scale of the problem is large. In an average year, even today, there are some 40 notifiable dust explosions world-wide, but the average number of fatalities has fortunately fallen to around one per year internationally thanks to the provision of modern design and safety procedures. This may be compared to around one dust explosion per working day in central Europe alone as recently as the 1960s.

3.1.2. Criteria for Initiating a Dust Deflagration

A dust deflagration may occur when all of the six conditions identified in Section 2 are simultaneously satisfied, and we will consider each of them in detail.

The dust must be combustible

It is obvious that any dusts formed primarily of carbon will be combustible, since the reaction of carbon with oxygen is thermodynamically favored and is exothermic. However, the form and purity of carbon is important, since these properties influence its reactivity. The fastest combustion of the particles is favored by the highest reactivity, and this is characterized by less pure forms containing volatile organic compounds, and by amorphous carbon rather than graphite in which the carbon-carbon chemical bonds are somewhat harder to break. Thus coal dust presents a much greater potential hazard than nuclear-grade graphite.

Other impurities, especially those which are already fully oxidized such as metal oxides, will not contribute to the oxidation process and may act as heat sinks, reducing or even extinguishing the reaction.

The role of catalysts is perhaps unexpected. Admixture of known catalytic materials with the carbonaceous dusts might be expected to increase the reaction rate (‘burning rate’ is also a common term in the literature of this subject and applies to the flame speed in the cloud of particles), and this would certainly be expected if the oxidation process followed 'Mode 1' kinetics (a free supply of oxygen or air with the rate controlled by the chemical kinetics, see [1]). However, this does not seem to be the case in experiments on nuclear material reviewed later in this report, and it useful to consider the mechanism in more detail in order to understand this.

These 'Mode' definitions were developed for solid graphite, which is porous, and 'Mode 1' assumes full penetration of air or oxygen into the porous structure: 'Mode 2', occurring as the temperature increases, sees some limitations imposed by the ability of oxygen to diffuse into that pore structure and the oxidation products to diffuse out; 'Mode 3' sees a further slowdown compared with the predictions of chemical kinetics as the reaction becomes limited by the available oxygen supply and the oxidation becomes confined to geometrical surfaces, and finally, at the highest temperatures, there is a noticeable acceleration in mass loss of carbon as the proportion of CO to CO_2 in the oxidation products increases (although some workers dispute this explanation). Catalysis is unimportant in 'Mode 3' since the chemical rate is not the dominant influence on the speed of reaction.

The question is how to compare the behavior of fine particles with that of solid material. One could argue that a dust suspension is like a *very* porous solid, but it seems more appropriate to consider that the fine particles are essentially *non-porous* and behave as individuals in terms of combustion but collectively in terms of heat transfer to initiate combustion in adjacent particles. This then makes the behavior quasi-Mode 3 and thus the low influence of catalysts more explicable.

Most of the relevant evidence comes from studies on coal dust, where it was established at an early stage that the initiating reaction occurred at the interface between the particles and the gaseous oxygen [10] and not through prior volatilization. Later work confirmed that the surface reactions were rate controlling but that heat transfer within and between particles was critical [11], with convection the primary mode of heat transfer in the pre-reaction zone (the next region to be enveloped by the flame front) whilst radiation was of secondary importance and conduction negligible.

In recent years, the modeling of not only the principal combustion process but of the overall dust explosion process has become very sophisticated. It is seen that the generalizations about particle behavior are insufficient on their own to model the very complex combustion process, and models need to consider heat transfer within the suspended dust cloud in considerable detail. The most recent models, *e.g.* [12], envisage a significant boundary layer between the particle and the bulk gas in which the concentrations of O_2, CO_2 and CO and the temperature change significantly, with all three modes of oxidation being invoked and the particle becoming simultaneously smaller and less dense.

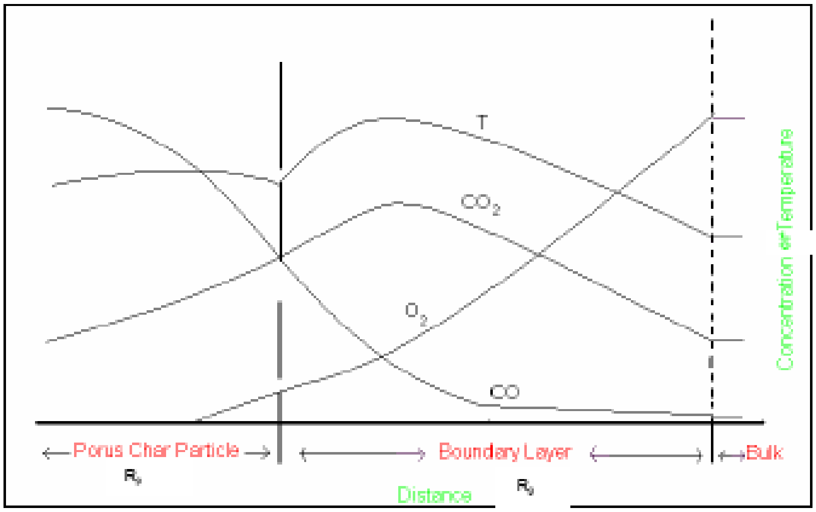

Figure 3-1
Changes in gas composition and temperature across the boundary layer between a porous carbon particle and the oxidizing gas atmosphere *(University of Leeds, UK)*

An expression may be derived for the overall particle burning rate or rate of carbon consumption per unit geometrical area of external surface of the particle, R_T:

$$R_T = C_g \left[\left(1 / R_{diff} \right) + \left(1 / R_c \right) \right]^{-1}$$

where R_{diff} is the rate which would be observed if the oxygen molecules were to react to form a gaseous product instantly on reaching the particle surface, and R_c is the corresponding rate if the oxygen molecules were to encounter negligible resistance in their transfer to the surface but them take a finite time to react. R_{diff} and R_c therefore represent the limiting mass-transfer-controlled and chemically-controlled rates respectively. R_{diff} dominates at high temperatures and for large particles whilst R_c dominates at lower temperatures and for small particles or for highly unreactive particles. C_g is the partial pressure of oxygen in the bulk gas – not that at the particle surface.

This has been developed further at Brown University (Rhode Island), where a kinetics model package has been produced [13] that describes carbon-particle oxidation, primarily for pulverized coal particles in power-station furnaces where it used to predict the amount of unburned carbon in the ash and so to optimize the process for maximum efficiency. Known as the Carbon Burnout Kinetic Model (CBK8), its full detail is beyond the scope of this review, it is worth noting that its main inputs are fuel properties (nature, particle size distribution, concentration in air, temperature, time, oxygen concentrations) and that it allows both for the build up of ash and also for any reduction in combustion efficiency brought about through thermal annealing (a significant problem for coal dusts bearing volatiles which may be removed ahead of the combustion of the carrier particle). The degree of oxygen penetration into the particle's porosity is monitored through the effectiveness factor and is a function of the Thiele modulus, and pore tortuosity is also allowed for.

The application of this model to nuclear graphite by the University of Leeds on behalf of UKAEA will be discussed in *Appendix A*.

In respect of volatiles content, which generally increases the deflagration risk, impurities with specific chemical groups such as –COOH, -OH, -NH_2, etc. are usually indicative of an increased potential hazard, whilst any halogen impurities tend to act as inhibitors. It used to be considered that carbon materials with less than 10% volatiles presented a negligible explosion risk [3], but the introduction of the ISO test standard has somewhat confused this picture.

We thus see that underlying the phrase "the dust must be combustible" is a vast body of research and knowledge of an exceedingly complex oxidation process where the outcome is often capable of being approximated by models but where the influence of all factors cannot always be foreseen precisely: thus, the science of dust deflagrations still depends heavily on practical tests utilizing standard methods to give comparisons between different dusts and condition.

The dust must be airborne

This aspect is straightforward: no suspended dust cloud, no deflagration risk. The conditions which can cause a dust suspension are either the introduction of a turbulent gas flow, causing disturbance of a settled collection of particles, or mechanical displacement of the material (*e.g.* during decommissioning activities) causing it to fall through an air-filled void space or to be thrown up into an air space. Very little quantitative work seems to have been done on this aspect of the issue although test methods have relied both on falling dust and on dusts blasted into a fixed volume using a sudden introduction of air.

The atmosphere must support combustion

In most cases in the nuclear industry we are considering either maintenance or decommissioning activities in which reactor systems contain air atmospheres. However, the possibility always exists to introduce deliberately an inert gas atmosphere if there is concern about a potential dust hazard – nitrogen (unless Magnox swarf is present) or argon are the most convenient options. However, utilization of inert atmospheres may be prevented in certain situations through consideration of worker safety in the immediate vicinity of the operations.

The particle size must be optimized for flame propagation

It is perhaps fairly obvious from the foregoing that the surface area of the solids present, which is available for heat transfer and oxidation, has a significant effect on the initiation and propagation of a dust deflagration. Any internal surface area is of course also important.

The process of size reduction in the particles as a result of chemical reaction is known as *comminution*. When this occurs, the specific surface area, which is the ratio of the external surface area plus any involved internal surface area to the total mass, increases, and the dust is able to burn more easily. It also becomes easier to disperse and to maintain in suspension. The increase in specific surface area can be very large – for spherical particles a reduction in size to one eighth of the original particle size (diameter) results in an 800% increase.

Thus, in general, a material generally becomes more hazardous as the particle size is reduced. Both the maximum explosion pressure and the maximum rate of rise of pressure increase as the particle size becomes smaller.

Some exceptions to this generalization can occur, especially where a solid oxide is formed which can remain associated with the particle. This is not the case with carbonaceous material unless it is extremely impure.

In normal circumstances, a range of particle sizes will exist, and the larger ones, with a much lower specific surface area, will tend to reduce the explosion hazard. They are also harder to maintain in suspension, and would require a more powerful ignition source.

Another common feature is that the more hazardous behavior of very small particles is mitigated by a tendency to agglomerate through cohesive forces.

A general 'rule-of-thumb' is that particles of any material in excess of 500 μm are unlikely to be responsible for the *initiation* of a dust deflagration, although they may participate in one. In the case of nuclear-grade graphite, we shall see later that this rule is followed rather precisely, and that only the smallest particles actually take part in the event whilst larger particles remain unburnt.

The dust concentration must fall within the explosible range

It is found that, just as with mixtures of explosible gases, combustible dusts admixed with air exhibit upper and lower 'explosion limits'.

The lower limit, classically referred to as the 'minimum explosible concentration', is the smallest quantity of suspended dust that is capable of initiating and propagating a flame, and is itself dependent upon the particle size. Below this minimum value, the particles are separated by distances such that the heat generated by one particle is insufficient to reach and ignite the next.

The upper limit, which is harder to define experimentally, is reached when the available oxygen supply is insufficient for the closely-packed particle cloud, and the flame propagation is quenched. The contribution of the high mass-per-unit-volume as a heat sink is also important.

These limits define the range in which, for a particular dust suspension with its own defined particle-size distribution, flame propagation is favored. Whilst one might expect that the most serious deflagration effects would occur with the stoichiometric concentration, this is generally not the case because almost all dust deflagrations leave a residue of unburnt or only partially burnt particles. In consequence, the more serious damage tends to occur with concentrations of particles which are in excess of the stoichiometric mixture.

Additional complications include inhomogeneity in the dust cloud (concentration *and* size distribution), together with the capability of the vessel or surroundings to act as a heat sink.

An ignition source of sufficient energy must be present

For a dust suspension to undergo *combustion*, a self-sustaining oxidation reaction allowing the progression of a flame front, there must first be *ignition*. In this context, *ignition* means the input of energy, by whatever means, at sufficient local concentration to initiate a combustion reaction at a point in the dust suspension which is locally self-sustaining. Dependent upon other parameters, the resulting flame front may propagate vigorously through the dust cloud or be extinguished after a short distance.

An *ignition source* may take many forms. The most obvious is a flame from an external source, such as a cutting tool. It may be a mechanical 'spark' from cutting or grinding metallic items: such sparks occur when the relative velocity of the cutter to the cut item exceeds about 1 $m.s^{-1}$. It can be seen that a falling object could exceed such a relative speed and so generate mechanical 'sparks' from a collision. The 'relative electrical energy' of such sparks may be assessed from a knowledge of their temperature and the involved materials. Electrical ignition sources may be electrical sparks on a small scale, or a larger electrical 'flash-over' resulting from some significant fault in adjacent apparatus.

An ignition source may simply be a hot surface on which some of the dust has collected, providing sufficient heat, perhaps over a lengthy period, for some of the collected dust to commence *smouldering* or *self-ignition* which then initiates the oxidation in an adjacent dust suspension. In many standard dust-deflagration assessment apparatuses, it may be a chemical igniter of specified energy.

The energy of the ignition source is a critical parameter. Clearly there is a minimum energy, below which the ignition event is insufficiently powerful to initiate combustion in the suspended dust. The energy required for this can also be defined in terms of a minimum ignition temperature, *i.e.* the minimum temperature at which flame propagation can occur. This temperature can be ambient temperature for pyrophoric dusts, rising to temperatures in excess of 900ºC in some cases. A typical temperature for coal dust might be around 600ºC [3], but it is, of course, strongly dependent on other parameters such as particle size and concentration.

For electrical sparks, the discharge time is important in additional to the total spark energy. A 'slow' event, with a lower rate of energy input, is less likely to initiate a flame front that a sharp higher-energy 'spike'.

In addition to these 'obvious' forms of ignition event, one should also be aware of the risks from the inadvertent introduction of incandescent material from external operations, from the possibility of sparks raised through friction or impact, unforeseen actions such as the introduction of portable lighting and viewing equipment without an assessment of the potential consequence, and the often underestimated risk of electrostatic discharges. These last have been the cause of many serious industrial incidents – perhaps around 10% of large-scale accidents, often from overlooking the build-up of 'streaming potential' in flowing systems such as pipes filling grain silos. A particular hazard is the presence of an insulated good conductor which can become charged through induction and then discharge unpredictably through the insulation to another conductor.

For addressing risks from electrical sparks and electrostatic discharges, prudent grounding arrangements may eliminate the risk. Resistance to ground of less than 10   should ensure the rapid dissipation of any potential charge build-up.

Ref [3] discusses ignition in much greater depth than is possible here. It is however useful to quote an important rule of thumb which is that system temperatures should generally be at least 50K below the perceived minimum ignition temperature of the dust suspension (and 20K below the ignition temperature of any adjacent deposited material).

All graphite-reactor decommissioning activities should include an assessment of all possible sources of ignition, even though the perceived risk of a deflagration is extremely low. If an ignition source is inevitable (*e.g.* metal-cutting is to be undertaken) then it is prudent to minimize or eliminate as many of the other relevant issues from the list given in Section 2.

Additional factors

In fully assessing the risk of a dust deflagration, a number of other parameters also merit attention:

3.1.2.1 Moisture Content

Moisture is often present in dusts, the amount depending upon the relative humidity of the surrounding atmosphere, the hydrophilicity of the dust and, in consequence, the history of the plant involved.

The coolant environment of a gas-cooled reactor is generally controlled either at a very low moisture content indeed (HTR, Magnox) or at a modest level of around 300 vpm (AGR) such that, at the point of formation during operation, any dusts are unlikely to be significantly affected by moisture since the graphite and coolant temperatures are elevated (200 -360ºC for Magnox, graphite at around 450ºC for AGR and in excess of 800ºC for HTR). However, a different situation may exist in old low-temperature air-cooled reactors such as the Windscale Piles in the UK, where no specific moisture control was in place, and in water-tube-cooled graphite-moderated reactors where different cover gases may be present.

Prior to decommissioning, reactors may have been standing in an air atmosphere for several years, or indeed for very long periods in excess of 48 years (Windscale Piles again), and moisture control may have been relaxed or non-existent. As the moisture content of a dust increases, it tends to become more cohesive and to agglomerate into larger particles or ‘clumps’ of material which are quite difficult to disperse in air subsequently, thereby tending to reduce the propensity to a deflagration. In addition, any moisture present will absorb heat from any ignition source or propagating flame front in the course of warming and vaporization, and this heat will no longer be available for the combustion process.

The net effect is to raise minimum ignition temperature, minimum ignition energy, and the minimum concentration limit for a deflagration.

3.1.2.2 Hybrid Mixtures With Flammable Gases

Mention of the use of cutting devices using flames raises the possibility of the injection of flammable gases into the dust-laden environment. As might be expected, this has a profound effect on the behavior of the dust suspension should ignition occur.

Generally, a combustible dust mixed with a flammable gas will deflagrate (or maybe explode) more violently than in air alone, even if the flammable gas is present below its own explosion limit in air. This effect is due to the faster burning rate (or flame-front velocity) of the gas compared with dust alone. The ignition energy and temperature of the hybrid mixture will be lower than for the dust alone, whilst the minimum explosible concentration of the dust will also be lower.

A further effect of admixing flammable gases is to increase the effective ‘explosibility’ of dusts: thus, something classified as ‘non explosible’ can become explosible in the presence of the gas, even at low concentration well below the theoretical explosion limit.

3.1.2.3 Primary and Secondary Explosions

The basic descriptions of the deflagration process given so far relate to a primary explosion. A secondary event can occur if the expanding gases create new turbulence in an adjacent area of the plant, or if the primary deflagration causes some rupture of the environment giving access to new dusts which become suspended, to additional air, etc. These additional dusts can then either become ignited by the original ignition source or by the products of the primary event.

Many of the more serious industrial accidents have been brought about through secondary explosions of far greater violence than the initiating primary event.

3.1.2.4 Impurities

As has already been mentioned, impurities can work both to increase the effects of a dust deflagration (*e.g.* organic matter producing volatiles) to as inerters / heat sinks (*e.g.* metal oxides).

All of these factors must be taken into account in the assessment of risk of dust deflagrations in general. Many of these features are discussed below in the context of nuclear-grade graphite dust.

3.2. Development of Measurement Techniques

3.2.1 Basic Inflammators

A brief description of the development of test methodologies for dust deflagrations is relevant here because a number of techniques have been used to study graphite-dust behavior, and because the change in methodology has led to a changed view on the “explosibility[5]” of graphite dusts which requires explanation.

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[5] ‘Explosibility’ remains the standard term in the literature when describing whether or not a particular dust cloud will participate in a deflagration, and is therefore retained where necessary in this text for the avoidance of confusion when citing literature references.

Initially, experimental work on assessing the propensity of particular dusts to deflagration risk proceeded independently in a number of countries, and the ultimate solution has been the introduction of a standard ISO test. However, this development process has had the unfortunate consequence of changing the ‘official’ classification of nuclear-grade graphites from ‘non-explosible’ to ‘weakly explosible’, and it is important to understand how and why this has come about.

Ref [3] has such pure forms of graphite explicitly defined as ‘non-explosible’. This was based on the early work conducted in the United Kingdom, and we therefore commence the survey there, noting an interesting historical compilation of the development of test procedures by Raftery [14] which was updated by Field [15].

There is a basic difficulty, which is to find a method of producing a consistently homogeneous suspension of dust at the required concentration under reproducible aerodynamic conditions. Generally, results are not very reproducible. A second difficulty is to ‘extrapolate’ tests conducted at laboratory scale to the volume and conditions of an industrial situation.

Early UK assessments were entirely based on the visual observation of flame propagation, using one of three types of apparatus:

(i) a vertical tube in which dust was dispersed vertically upwards and containing an electrically-heated coil or electrodes for a spark;

(ii) a horizontal tube with the dust blown along it past a platinum-wire coil heated to 1300ºC; *and*

(iii) the *‘inflammator’*, a vertical tube similar to (i) but with the dust dispersed vertically downwards.

The vertical apparatus in (i) was similar to the so-called Hartmann apparatus developed by the US Bureau of Mines. When the coil was used, this consisted of around eight turns of Kanthal wire heated to approximately 1000ºC (bright-red heat) using approximately 10V at 20 amps. The electrical spark bridged a 5 mm gap and was produced from a 10kV 0.024 amp transformer.

Typically, 0.5g of dust would be placed in a small cup and then blown upwards either by a pulse of air of a continuous blast. The ignition sources were activated continuously and, if any evidence of flame propagation was seen, the dust was classified ‘explosible’. Dusts which were initially ‘non-explosible’ were varied in different ways – quantity, drying, sieving, etc. to explore a wider range of conditions. Ref [3] includes photographs of ‘mushroom-cloud’-style flame balls emerging from the top of the glass or Perspex tube for clearly explosible materials such as wheat flour. Pure graphite dust was always ‘non-explosible’ in these conditions.

The horizontal apparatus in (ii) consisted of a glass tube with a standard internal diameter (in the UK) of 64mm and was 1.5 m in length. The coil was at the same temperature as in (i). Around 2g of the dust would be placed in a ‘conical heap’ around 350mm from the coil and then blasted over it with pulses of air directed at the base of the heap.

The ‘inflammator’ (iii) was a similar but shorter glass tube (1m) mounted vertically. The principal difference was that the dust (approx 2g) was allowed to fall under gravity.

All three apparatuses were used in the UK in order to explore the range of conditions before a dust was finally classified either as ‘explosible’ or ‘non explosible’.

The equivalent US tests on the basic explosibility of carbonaceous materials are documented in [16]. Unlike the UK, a straight “yes/no” classification of explosibility was never adopted. Instead, a ‘relative explosion hazard rating’ was employed, based upon data on minimum ignition temperature, minimum explosible concentration, minimum ignition energy, minimum explosion pressure, and maximum rate of pressure rise. Everything was related to a particular grade of Pittsburgh coal, and two terms were defined:

$$\textit{ignition sensitivity} = \frac{\textit{min. ign. temp} \times \textit{min ign. energy} \times \textit{min. explosible concn.}_{\textit{(Pittsburgh coal)}}}{\textit{min. ign. temp} \times \textit{min. ign. energy} \times \textit{min. explosible concn.}_{\textit{(Sample)}}}$$

$$\textit{explosion severity} = \frac{\textit{max. expl. pressure} \times \textit{max. rate of pressure rise}_{\textit{(Sample)}}}{\textit{max. expl. pressure} \times \textit{max rate of pressure rise}_{\textit{(Pittsburgh coal)}}}$$

… each term being determined at a concentration of 500 g.m^{-3}. The two terms were then multiplied together:

$$\textit{explosion index} = \textit{ignition sensitivity} \times \textit{explosion severity}$$

The major drawback of this system was the need to measure numerous parameters before any ‘rating’ could be obtained.

Before discussing the techniques developed in both UK and USA to determine these parameters, it is worth mentioning the important contributions of a number of other European countries. Norway, in particular, has established at the Christien Michelsen Institute one of the leading organizations in dust-explosion research following a series of serious grain-silo accidents in the 1970s. This institute developed its own style of flame-test apparatus consisting of a vertical tube using an acetylene burner as the ignition source for an upward dispersal of dust using air injection. However, it is the measurement of more specific parameters, in particular minimum ignition energies, that this institute has made its major contribution and we shall also include developments in Switzerland and Germany within the examination of specific measurements of these individual parameters.

3.2.2 Parameter Measurement

3.2.2.1 Minimum Ignition Temperature

A rather crude apparatus has been utilized for many extant literature measurements of this parameter. It consists of a tube furnace mounted vertically around a Vitreosil tube and initially set at 500ºC. Approximately 0.2 g of dust in then forced down through the furnace using an air blast. If flames are observed at the bottom of the furnace, then clearly the dust has ignited. Conditions are then varied, with the furnace temperature progressively reduced, to find the minimum temperature at which flame propagation occurs.

One significant feature of this test is that some dusts classified as ‘non explosible’ may nonetheless ignite, and possess a minimum ignition temperature.

European convention is to set a temperature 10 – 20K *lower* that the observed minimum temperature of flame propagation as the assumed value in any safety assessment.

3.2.2.2 Minimum Explosible Concentration

This has been determined in the UK using the basic vertical tube apparatus (as in (i) in Section 3.2.1 above) with an electrical spark as igniter, since very small amounts of dust were found to stick to the heated-coil design. Sometimes the top of the tube would be sealed with a paper diaphragm to avoid loss of very low density material. The result was again determined by visual observation, usually in a darkened environment because of the very low flame intensities observed.

The Norwegians used a much more sophisticated system, developing the use of large spherical vessels for this measurement and other tests [17]. Their standard method used a 15 litre spherical vessel and a 100-200 watt electric arc of duration 0.1 – 0.4 seconds, the dust being suspended by a blast of air. The criteria for flame propagation was that a distance of 100mm or more should be achieved. The relevant dust concentration was determined by a dummy run with dust suspension but no ignition, with a rapid collection of 200 cm^3 of the suspension from the central area of the apparatus and weighing the dust on a filter. The minimum concentration was assessed on a probability basis over a number of runs, the concentration of dust which gave an explosion probability of 0.5 being regarded as the minimum explosible concentration, assessed as the arithmetic mean of five independent assessments.

In Switzerland, Bartknecht (see, *e.g.* [7]) also pursued the philosophy of using large vessels, believing that the use of small tubes resulting in significant underestimates of potential risk. These vessels introduced the use of chemical igniters, typically of 10,000 J, which have the disadvantage of creating their own pressure pulse which needs to be taken into account in analyzing results. For the assessment of minimum explosible concentration, vessels of either 20 litre or 1 m^3 were generally used; comparison with a blank test (one containing just the igniters, and no dust) were used to assess the presence of a dust explosion of the pressure/time trace.

3.2.2.3 Minimum Ignition Energy

The most important developments in determining this parameter are due to Eckhoff in Norway [18] using his spark apparatus. He considered that if the discharge time of the spark was long enough to reduce the ‘shock-wave’ effect on the dust, then very low ignition energies could be determined using the US-type Hartmann apparatus. Ignition energy was controlled from banks of capacitors to produce energies in the range 0.3 mJ – 7.5 J, with the probability of ignition being plotted against ignition energy once the ‘optimum’ conditions of dispersion and spark duration had been determined.

The British used a similar apparatus over a smaller range of spark energies, progressively reducing the energy to a point where no explosions occurred over at least ten consecutive tests. Shortcomings in the method were recognized, especially in the reproducibility of the spark circuitry, and some further work was undertaken which led to the introduction of a British Standard [19] relating to the control of static electricity in dust-laden environments: however, the work remained generally inferior to that of Eckhoff.

3.2.2.4 Maximum Permissible Oxygen Concentration to Prevent Ignition

This parameter is of interest where control of the atmosphere is feasible, and a basic test was developed simply by altering gas compositions in a vertical tube apparatus partially sealed with a lid.

Two much more important parameters are:

3.2.2.5 Maximum Explosion Pressure and Maximum Rate of Pressure Rise

……… and these are now considered in the context of the development of a standard ISO test methodology for the characterization of dust deflagration events.

Much of the foregoing is usefully compiled in Section3, Chapter 12, of the US Fire Protection Handbook [20].

3.2.3 Development of ISO and ASTM Standard Tests

A modern test capable of scrutiny by nuclear-industry standards of quality assurance cannot be based upon visual observations of flame propagation, although such tests retain considerable value for demonstrating principles, as will be seen later in the work on nuclear graphite analyzed in this review.

Evaluation of essential parameters such as explosion pressure and rate of rise of pressure require sophisticated instrumentation, and there have been two principal stages in the development of standard equipment.

The first of these is a strengthened and sealed version of the US style of vertical tube apparatus, known as the ‘Hartmann Bomb’, with spark or hot-coil igniters (UK), or just the electric arc (Norway). In the US both have been used, along with guncotton for dusts which are difficult to ignite. A known quantity of dust is injected using a known quantity of high pressure air, and the concentration calculated on the assumption that the dispersion is uniform. Pressure transducers record the progress of any deflagration as a function of time.

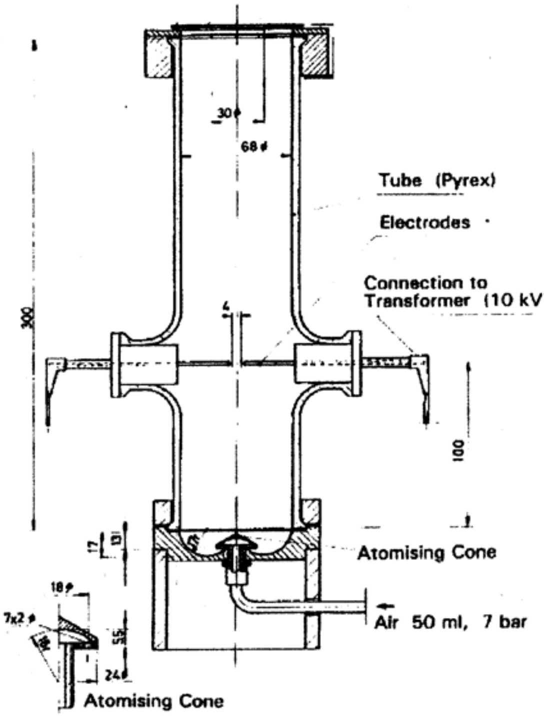

Figure 3-2
Simplified Diagram of the ‘Hartmann Bomb’

These initially rather crude assessments have been developed around the spherical vessels favored by the Swiss, and the current ISO standard method [21] is a further development utilizing (usually) a 1 m^3 standard vessel whilst the equivalent ASTM standards for individual measurements utilize the '20-litre vessel or larger' [*e.g.* 22, 23]. We confine the detailed description here to the ISO standard[6]: in all respects except for vessel size the methodologies are comparable.

The dust to be tested is placed in a secondary container of about 5 litre volume, pressurized to 20 bar with air. The dust is injected into the main spherical vessel via a semi-circular spray pipe when a fast-acting valve is activated. The initial pressure in the main vessel is slightly below atmospheric pressure such that, when the injection is just completed, the pressure equalizes at 1 atmosphere.

At the centre of the main vessel are two pyrotechnic igniters consisting of a mixture of zirconium, barium nitrate and barium peroxide, generally of total energy 10 kJ. This energy can be calculated rather precisely from the known thermochemical data relating to the reactions. These igniters, as already mentioned, represent a significant energy input of their own and generate a pressure pulse which must be characterized and eventually 'deducted' from the observed behavior in any test, in order to provide data representative of the test sample.

Rigorously, the ISO standard is limited to *determination of explosion indices* (or deflagration indices) in air, as defined in Section 3.1.1, although the standard apparatus, suitably instrumented, is capable of delivering important data on flame propagation and temperature. There is also, in the present authors' view, a significant weakness in the ISO standard, in that its 'Field of Application' statement contains the following caveat:

"If the specified experimental procedure.....does not result in ignition of the dust/air mixture, it should not be concluded that the dust in question cannot explode. The interpretation of such cases should be left to specialists in the field of explosions and explosion protection."

Thus, the interpretation of the test for any weakly-explosible or non-explosible substance (such as nuclear-grade graphites) is to be left to the subjective judgment of individuals.

Within the written standard, the 'staub' suffix 'st' on the deflagration (or explosion) index is not used, and a different definition K_{max} is introduced, representing the worst possible value of the index over a range of experimental conditions, principally reactant concentration. There is also introduced a turbulence index t_V which relates to the ignition delay after the particle injection, and a second turbulence index T_u which is used to compare the index obtained at a specified degree of turbulence to that under quiescent conditions. These details will not be further elaborated here.

Particle sizes for the ISO test must not exceed 63 μm, and the moisture content of the dust must not exceed 10%. The 10 kJ chemical igniters are located at the centre of the spherical vessel. A practical version of this apparatus is shown in Figure 3-3:

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[6] A German standard, VDI 3673 (October 1983) is very similar to the ASTM standard, utilising a 20-litre vessel and giving equivalent definitions: a later publication, AFNOR U 54-540 (December 1986) chooses to use the expression K_{max} instead of K_{st}: this is defined below.

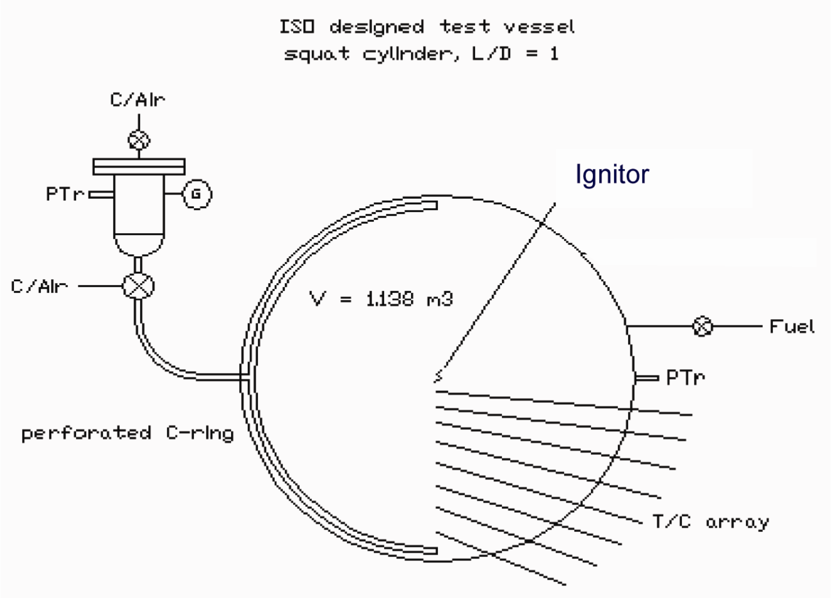

Figure 3-3
Practical version of the ISO standard apparatus for the determination of deflagration index and additional parameters, as used at the University of Leeds (UK) Energy and Resources Research Institute

The ISO standard considers that the accuracy of a maximum explosion pressure produced in this way is ±4%, whilst the standard deviation on a maximum deflagration index measurement falls non-linearly from around 10% when K_{max} is of order 200 bar.m.s^{-1} to around 6% when K_{max} is 400 bar.m.s^{-1}.

It may be noted that a relatively low peak explosion pressure normally indicates a poor combustion efficiency – *i.e.* that a significant proportion of the dust has not reacted. It clearly emerges from the work to be described that graphite is such a material, and therefore greater reliance should be placed on the values of K_{st} as a determining parameter in the current review. K_{st} values are normalized for different vessels utilizing the cube root of the volume of the vessel (see below). The evaluation is based upon the supposition that events within the vessel are entirely homogeneous and, as shall be demonstrated later, this is not entirely true.

Comprehensive illustrations of the data obtained from this apparatus are given in the analysis of UK data on nuclear graphite dusts, Section 4.4.2.

The practical result of the development of testing methodologies for dust deflagration over the years has been to move from very simple apparatuses dependent upon subjective operator assessment of the outcome to a standard apparatus in which a high-powered chemical explosion always occurs and from which the true behavior of the test sample needs to be de-convoluted. In no sense is either of these extremes satisfactory. This situation is, unfortunately, the inevitable result of the extreme difficulty of creating and reproducing a dust suspension with quantifiable parameters in order to evaluate other parameters which are very sensitive to small changes in conditions.

The perceived value of the ISO test is for the comparison of different types of dust under identical conditions. As an absolute indicator for weakly- or non-explosible dusts, given the presence of the large ignition energy and pressure pulses arising from the chemical ignitors, its value is doubtful. The consequence of the application of the ISO standard for nuclear-grade graphite is that it becomes classified as weakly explosible[7], despite the need for a flammable-gas driver in the Leeds 'ISO' apparatus shown in Figure 3-3 to obtain any kind of reproducible deflagration with a PGA graphite dust sample.

In conclusion of this review of testing methodologies, a further reference [24] is drawn to the reader's attention which, under the general title of "Prevent Explosions of Combustible Dusts" seeks to relate these principles in general terms to the industrial situation, covering the risk associated with dust layers as well as with suspended materials. Curiously, this otherwise useful summary avoids all mention of the ISO standard.

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[7] largely on the basis that, in the presence of the chemical igniters, it is impossible to say that it is not.

4

THE PRINCIPAL EXPERIMENTAL STUDIES ON DUST DEFLAGRATION TO SUPPORT REACTOR OPERATION AND DECOMMISSIONING

4.1 Introductory Remarks

In this course of collecting data for this review, it has been very noticeable that very little consideration has been given to the possibility of any threat of fire or explosion from graphitic or carbonaceous dusts during the operational lifetimes of graphite-moderated nuclear plant. Given that there were problems of various kinds with such dusts – concerns about frictional wear of graphite components (found to have been greatly exaggerated), formation of non-graphite 'sooty' deposits of various kinds on the tubing of steam-generating units, structural steelwork and on fuel elements, similar deposits affecting graphite fuel sleeves which were sufficient to 'glue' adjacent sleeves together (in UK AGRs) and to cause major infilling between sleeves and fuel elements (Tokai 1 Magnox reactor) – and that significant research programs were dedicated to investigating the chemical causes and potential alleviations achievable through modification to coolant composition, this is perhaps quite surprising. A number of background papers on these issues are collected in [25].

Some reassurances were available that dusts were not circulating widely in the coolant: the installation of circumferential inertial collectors (CICs) in selected UK AGR fuel channels, which were expected to collect and control the extent of such circulating graphitic and metal-oxide material, was suspended when it was found that very little of significance was collecting in them. Routine maintenance periods with man access to peripheral parts of the coolant circuits also found little evidence for the large-scale generation and transport of dusts.

In the UK, a suspended-dust-cooled reactor design had even been contemplated (see sub-section 4.4.1).

It was not until the aftermath of the Chernobyl accident that safety authorities and regulators started to take notice of graphite oxidation properties, and they have subsequently mistakenly identified even solid graphite components as a 'fire hazard'. Ref [1] deals with these issues at great length.

Questions about the behavior of graphite and carbonaceous dusts have followed, and have not been so easy to address on the basis of archived and literature information These have largely been raised in connection with the planned decommissioning of graphite-moderated reactors in the UK, France, Italy and Japan, and have led in each case to some comprehensive work programs designed to build upon the basic understanding of the behaviors of such dusts gleaned from the early work on carbonaceous materials which has been outlined in Section 3.

With the cooperation of UKAEA, EdF, SoGIN and NUPEC on behalf of JAPC, much of this work has now been brought together in this comprehensive analysis. The various work programs have explored different aspects of the issue, but with sufficient commonality that the results may be combined together to give a convincing picture of the essentially innocuous nature of the dusts which might be encountered in decommissioning.

A further consequence of the post-Chernobyl interest is that designers of new reactors are now giving thought to the implications of graphitic dust generation in their systems, to ensure that operating and eventual decommissioning safety cases are well prepared to address any concerns which may be raised in the future. The recent international work programs of course provide just the support which is required.

We begin with individual descriptions of the identified research programs in Italy, Japan, the United Kingdom and France, bringing in other evidence (*e.g.* from graphite manufacturers) as appropriate. It is convenient to start with Italy and Japan, where the work is largely confined to measurements of the kind which have already been described.

4.2 Italy

SoGIN have conducted or commissioned work utilizing both unirradiated graphite dust prepared from core material archived at the Latina reactor site and irradiated circuit dusts conducted over a lengthy period of operation of the reactor. The work on dusts has been integrated with a programme of practical work on the Latina site studying the effects of gas torches on the behavior (particularly temperature changes) in adjacent graphite blocks: this latter work is not discussed further here, but it the subject of two long video recordings which clearly illustrate the benign nature of bulk graphite even when high-temperature gas torches impinge upon it for long periods. The videos also cover some basic work using dust, which is described here.

Parametric work on the dusts was conducted by Stazione Sperimentale per I Combustibili, a specialist combustion laboratory located at San Donato near Milan. However, for the studies on irradiated material, the apparatus was transported to the Latina site for the duration of the study, and subsequently successfully decontaminated and returned to the Milan laboratory.

4.2.1 Initial Studies Using Bulk Graphite Powder (Unirradiated)

The initial studies are described in a SoGIN internal report [26]. Powdered graphite was prepared on the Latina site by grinding and sieving a quantity of unirradiated moderator material (UK-manufactured Pile Grade ‘A’ graphite from the Anglo Great Lakes Co.). It was desired to simulate cutting operations during decommissioning with the expectation that quantities of dust might lie on top of the graphite core and become affected by adjacent cutting operations using flame or by the consequent white-hot metal swarf.

A bed of graphite keys weighing approximately 28.5 kg was laid in a steel tray to simulate the top of the reactor core, and some 13 kg of graphite was spread across this in an even layer. Three thermocouples were embedded in the powder and in the underlying graphite components to monitor any significant temperature changes.

Initially, a piece of sheet metal was cut with a plasma lance held above the tray of graphite powder. After ten minutes of cutting, the effect on the graphite was effectively zero. An oxy-acetylene torch was then introduced. This was passed back and forth across the graphite powder, producing a little local incandescence. Over a period of 20 minutes, the embedded thermocouples registered less than 50K increase whilst the local temperature in the powder bed in the zone where the flame was 'scanned' across it never exceeded 200ºC. At twenty minutes there were no further changes in temperature and so the test was terminated.

A second test utilizing the same equipment was conducted after 240 g of oil had been distributed over the graphite powder and left to soak in. An additional 15 g of oil was spread across the surface of the bed immediately before the test commenced. The total oil content was approximately 6000 $\mu g.g^{-1}$ (0.6% by weight). Thermocouples were placed in the dust at the point where the swarf from the metal cutting fell on to the dust. In the first few minutes of this test, some fuming of the oil was noted with some brief ignition and visible flame. However, this had no effect on the graphite powder and, after this initial phase, the overall behavior of the dust and graphite bed was similar to that in the first phase of the test, indicating that the presence of oil did not appear to significantly increase the risk of any combustion in the dust.

The video which accompanied this test also provides evidence of thermocouple readings by filming the chart recorders. The video record then moves on to some tests involving bulk graphite blocks, again with oil added at a second stage and again giving an innocuous result, and then continues to a separate test using suspended dust which is also reported in [26].

A box approximately 1 m^3 was prepared, with about 1 kg of graphite dust deposited in its base. A Vitreosil viewing window was available in one wall of the box, and through the opposite wall an aperture was provided through which an oxy-acetylene torch was introduced. In the top of the box, four holes were introduced to relieve any internal pressure which might have been generated. The holes also served to allow the insertion of four thermocouples to monitor the temperature at different heights in the box. The amount of graphite was increased to 2344 g to give a concentration in the range 100 – 200 $g.m^{-2}$ (this is presumed to be per square meter of the base of the box, and regarded as typical of what might be encountered during decommissioning: to the present authors this estimate appears unrealistically high).

The powder was suspended with a brief air blast and then the flame was introduced. It was considered that the gas emissions from the torch were sufficient to keep about 50% of the powder in suspension.

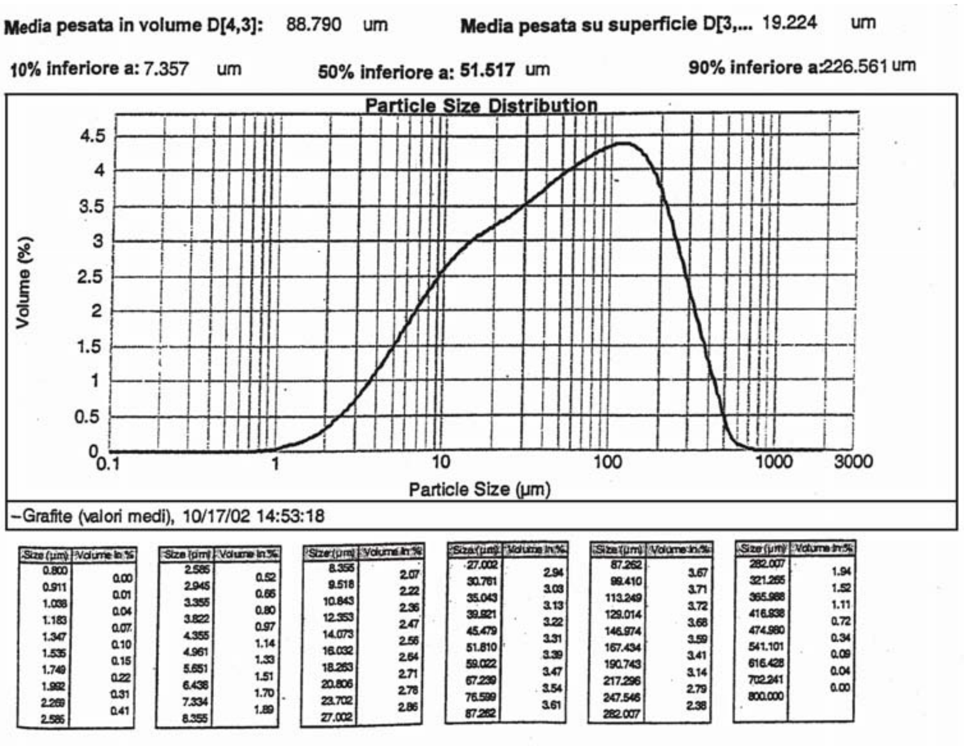
In a period of approximately 10 minutes there was 'no manifestation of a phenomena worthy of consideration', notwithstanding further injections of air to maintain the suspension. The internal temperature of the box rose to about 150ºC. After the test was concluded, the quantity of graphite powder remaining was 2091 g, the balance presumably lost through quiescent oxidation in the vicinity of the flame.

This somewhat dramatic method of addressing the potential explosibility of the dust in a confined space has merit in that it was a practical reconstruction of circumstances which could arise directly in a decommissioning scenario, giving a comforting indication of the benign nature of the suspended dust which does not depend on the interpretation of parameters determined by specific test procedures in situations which are non-realistic from the decommissioning point of view.

However, knowing the values of these ‘standard’ parameters for this powder which was clearly benign in a practical situation also adds greatly to the overall understanding, and indeed to the interpretation of similar parametric measurements on other graphite dust samples from other sources. The Italian colleagues therefore decided to have specific measurements made by a specialist laboratory and these are described in the following sub-section.

4.2.2 Studies by Stazione Sperimentale per i Combustibili

Two series of measurements were made by Stazione Sperimentale per i Combustibili (‘SSC’): an initial series of measurements on the same unirradiated powder as used in 4.2.1, reported in [27], and measurements on irradiated dusts recovered from the gas circuit of the Latina reactor, reported in [28]. The overall results are summarized by a SoGIN analysis [29]. We begin with the data on the unirradiated graphite powder, prepared on the Latina reactor site, for which a particle-size distribution was obtained using a Malvern Instruments (UK) ‘*Mastersizer 2000*’ which utilizes diffraction from either a He/Ne laser at 633 nm or a diode laser at 450 nm. The results show a wide-ranging particle size with 10% below 7.3 μm, 50% below 51.5 μm and 10% above 226 μm (Figure 4-1).



Media pesata in volume D[4,3]: 88.790 um **Media pesata su superficie D[3,...** 19.224 um

10% inferiore a: 7.357 um **50% inferiore a: 51.517** um **90% inferiore a:**226.561 um

Size (µm)	Volume In %
0.800	0.00
0.911	0.01
1.038	0.04
1.183	0.07
1.347	0.10
1.535	0.15
1.749	0.22
1.992	0.31
2.269	0.41
2.585	

Size (µm)	Volume In %
2.585	0.52
2.945	0.66
3.355	0.80
3.822	0.97
4.355	1.14
4.961	1.33
5.651	1.51
6.438	1.70
7.334	1.89
8.355	

Size (µm)	Volume In %
8.355	2.07
9.518	2.22
10.843	2.36
12.353	2.47
14.073	2.56
16.032	2.64
18.263	2.71
20.806	2.78
23.702	2.86
27.002	

Size (µm)	Volume In %
27.002	2.94
30.761	3.03
35.043	3.13
39.921	3.22
45.479	3.31
51.810	3.39
59.022	3.47
67.239	3.54
76.599	3.61
87.262	

Size (µm)	Volume In %
87.262	3.67
99.410	3.71
113.249	3.72
129.014	3.68
146.974	3.59
167.434	3.41
190.743	3.14
217.296	2.79
247.546	2.38
282.007	

Size (µm)	Volume In %
282.007	1.94
321.265	1.52
365.988	1.11
416.938	0.72
474.980	0.34
541.101	0.09
616.428	0.04
702.241	0.00
800.000	

Figure 4-1
Particle-Size Distribution of Unirradiated Graphite Dust Representative of Latina

The above result is the mean of nine separate determinations.
The parametric measurements[8] on this material were as follows:

4.2.2.1 Minimum Ignition Temperature (described in [27] as 'lower limit of flammability')

The apparatus used for these measurements was essentially a well-instrumented Hartmann bomb of volume 2.3 litre, using an incandescent coil at approximately 1350ºC as ignition source, the tube closed at the upper end with a bursting disc and maintained at the desired temperature using a heating mantle, and with he test dust initially placed in a cup at the base of the instrument before suspension using an air pulse.

SSC consider a dust to be explosible[9] under specific conditions 'on a statistical basis' if a flame which is initiated at the base of the dust suspension propagates through the whole reactor volume with a corresponding increase in pressure. The quantities of dust used ranged from 200 – 3000 mg, representing concentrations in the range 86 – 1293 g.m^{-3}. The tests were conducted at ambient temperature and at approximately atmospheric pressure. In *no* case did any deflagration result, and SSC therefore classified the unirradiated Latina graphite dust as *non-flammable*.

<u>Explosion parameters</u> *(Maximum explosion pressure and maximum rate of pressure rise)*

These tests were conducted using ASTM E1226 procedures in a 20-litre vessel [23], utilizing a standard instrument from the Swiss manufacturer Adolf Kühner AG (Figure 4-2).

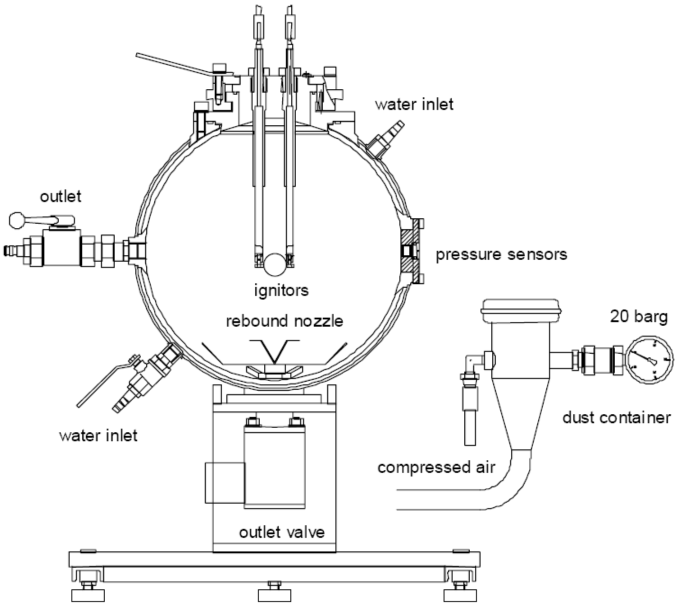


Figure 4-2
A. Kühner 20-litre Vessel as Used in the Italian Studies

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[8] the tests also included electrical resistivity, but this is not discussed here

[9] they use the term 'flammable' and state that the term is synonymous with 'explosible', although the present authors disagree

Two 5kJ igniters were used providing a total 10 kJ ignition energy. Ref [27] reports the following explosion indices for this material:

Max explosion pressure:	5.43 bar
Max rate of pressure rise:	118 bar.s^{-1}
K_{st}:	32 bar.m.s^{-1}

From the published figures which accompany the report, it is not immediately obvious how these numbers are derived, especially the maximum rate of pressure rise:

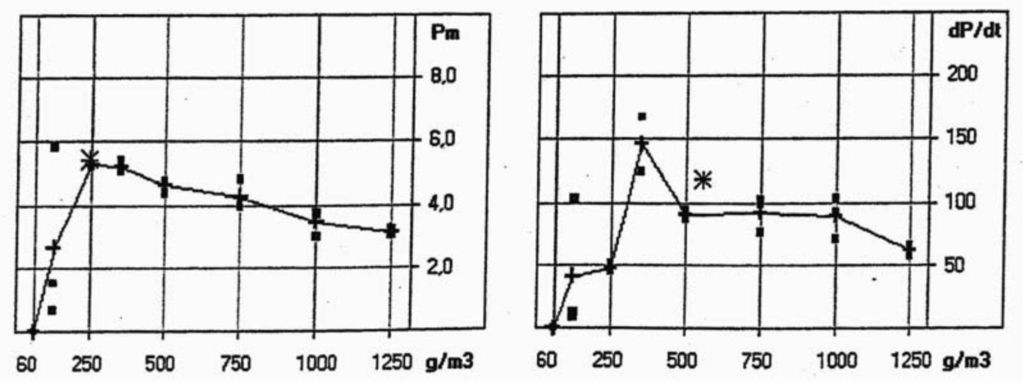


Figure 4-3
Explosion Parameters Derived by SSC for Unirradiated Latina Graphite Powder

The identified explosion indices are shown on Figure 4-3 by the 'star' symbols. In the case of the maximum rate of pressure rise, this appears not to be the maximum and it also appears to lie *outside* the main range of data.

Consultation with SoGIN reveals that this situation arises, at least in part, through rigorous application of the ASTM E-1226 procedures as further elaborated in the Kühner company operating-procedure documentation. Initially, the parameters are determined over a wide range of dust concentrations (this is 'test series 1' in the SSC table of results which is reproduced below). In this instance, this covers the concentration range 60 – 1250 g.m^3. The ASTM then requires that the concentration range close to the observed maxima in explosion pressure and rate of pressure rise shall be repeated (usually the actual concentration and those immediately below and above), and that the explosion indices shall then be calculated as the mean values of the *maximum* values of the three series of tests. In fact, the results represented by the 'star' symbols are close to the average values obtained from *all* data taken together, which are 5.34 bar for the mean value of the maximum explosion pressure, and

119.6 bar s^{-1} for the mean value of the maximum rate of pressure rise.

These data place the results well within the upper bound for formal classification St_1 "weakly explosible".

In this work by SSC, the second and third series of tests were widened to cover the range 125 – 1250 g.m^{-3} because the operators noticed that the maxima appeared to be shifting in comparison with the first series of tests. They also performed two additional tests ('series 4') for confirmation purposes.

The following table shows the data exactly as reported in [27]:

Series	Test No.	Concentration of Dust (g.m^{-3})	Max Explosion Pressure (bar)	Max Rate of Pressure Rise (bar.s^{-1})	t1 (ms)	t_v eff (ms)
1	1	750	4.8	98	90	59
1	2	1000	3.8	71	100	60
1	3	1250	3.2	66	**88**	59
1	4	500	4.4	94	**88**	60
2	5	500	4.8	87	91	59
2	6	750	4.1	**101**	**74**	60
2	7	1000	3.0	93	215	59
2	8	250	**5.2**	51	192	60
3	9	250	**5.3**	45	204	60
3	10	500	4.7	89	113	60
3	11	750	4.0	76	101	60
3	12	1000	3.7	**103**	**71**	60
3	13	1250	3.1	58	121	59
1	14	125	**5.8**	**103**	96	60
1	15	60	0	0	303	59
2	16	125	0.7	13	279	60
3	17	125	1.5	8	415	59
4	18	350	5.4	124	93	60
4	19	350	5.0	**167**	**90**	60

The highlighted data (as in the original) are the maximum values found in each series of tests, and are those from which the average quoted values have been derived (for the turbulence parameter it is the minimum rather than the maximum which is significant), in apparent conformity with the requirements of the test standard. Logically this suggests perhaps that the characteristics of the powder were varying during the test sequence: it may well appear illogical that the highest value found is not the highest value reported, and that some high test results are not part of the averaging process. It is certainly not clear why SSC resolved to include test 19 rather than 18 unless the decision was based upon the value of the turbulence parameter.

The whole data set will be taken into consideration in the analysis of the total collection of data from different countries.

4.2.3 Auto-ignition Temperature

This test utilizes the downward-facing vertical tube, and samples were prepared of powder with granulometry below 75 μm in 100 mg aliquots. The vessel could be heated to a maximum of 600ºC utilizing a heating mantle and tests were performed with increasing temperature, controllable at intervals of 10K.

As described earlier, this test is considered positive when a flame emerges from the base of the tube when the sample is injected. In this instance, no ignition occurred at any temperature up to 600ºC. Initial tests were conducted at 300ºC, and the temperature was increased in 50K intervals in an attempt to find a positive result. As this did not occur, larger concentrations of graphite dust were also tried up to a maximum of 1000 mg. As a result, the graphite dust is reported by SSC as being *non-flammable* under the conditions of this test.

Minimum ignition energy

This test was conducted in a modified Hartmann apparatus constructed of silica glass and with an internal volume of 1.2 litres. This apparatus is also a product of Adolf Kühner and is known as '*MIKE 3*'.

A capacitor system allows the generation of spark energies of 1, 3, 10, 30, 100, 300 and 1000 mJ. A typical test for an explosible dust sees 900 mg of the dust dispersed and then sparked with a time delay of 120 ms. No ignition was possible up to the maximum spark energy of 1J.

Further tests were then conducted with chemical igniters. These tests were conducted with a range of ignition energies and at concentrations of 350, 500 and 750 $g.m^{-3}$. For 350 $g.m^{-3}$ it was found that ignition occurred at 2000 J and above, but not at 1000J: the same result was obtained in a smaller number of tests with 500 $g.m^{-3}$, whilst at 750 $g.m^{-3}$, 1500 J failed to ignite the graphite whereas 2000 J gave a positive result. 2000J thus appears to be a threshold value at all concentrations tested.

Susceptibility to self-ignition

This test was conducted using a standard applied to the transport of dangerous goods [30]. This utilized (at SSC) a temperature-programmed gas chromatograph to provide a furnace environment, and the sample was placed in a wire net carrier in the form of a cube of 10 cm side in the furnace which was initially at ambient temperature. The furnace was temperature programmed and the temperature was raised at 0.5 $K.min^{-1}$ until 140ºC was reached: this temperature was then held for 24 hours: a material is considered to be capable of auto-ignition if the temperature within the sample exceeds 200ºC during this period.

Not only did the sample not demonstrate this behavior, the temperature of the furnace was then slowly raised over the following 48 hours and the sample temperature remained *below* that of the furnace (Figure 4-4):

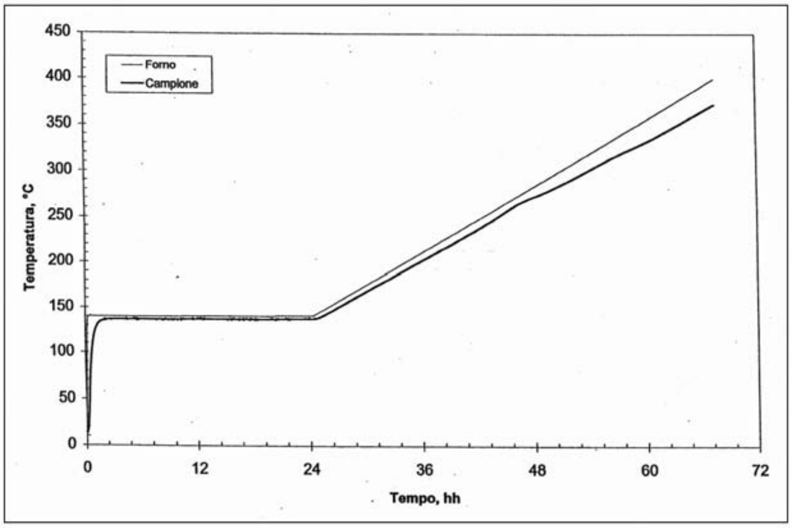


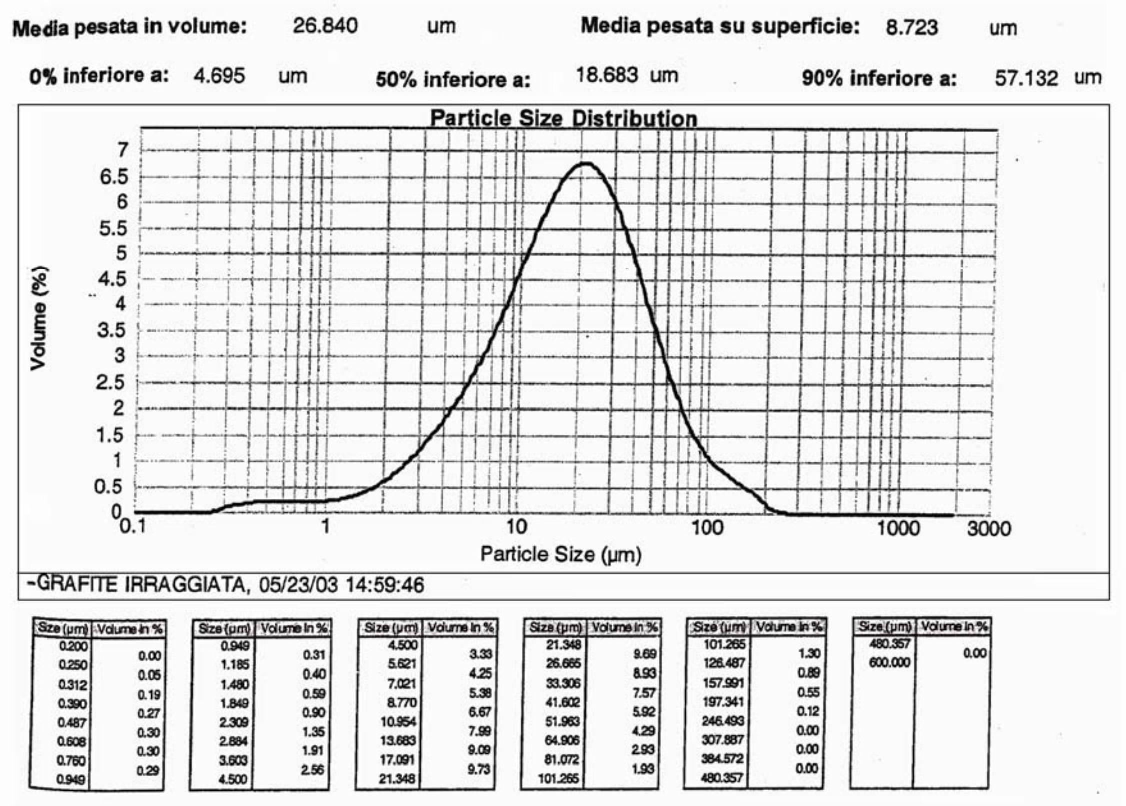
Figure 4-4
Temperature-programmed heating of Latina graphite dust sample to test for auto-ignition

On the basis of this result, SSC characterized the Latina virgin graphite-dust sample as non-susceptible to auto-ignition. This is consistent with the view of Field [3] who notes that “materials prone to spontaneous combustion are often chemically unsaturated and may be combined with another material which acts as a catalyst to the oxidative degeneration” – clearly pure graphite powder satisfies neither of these criteria.

Ref [28] from SSC covers tests performed on the so-called ‘irradiated graphite’. This is perhaps a misnomer, in the sense that this was material recovered from a filtration system within the Latina reactor which had collected material over a period of 21 calendar years during which the reactor operated for a total of 10.1 full-power years. The filtration system yielded 210 kg of blackish material, representing a collection rate of approximately 57 $g.full\text{-}power\ day^{-1}$. Indeed, [28] suggests that the substance was a mixture containing graphite (and possibly other carbonaceous deposits), Magnox, and metal oxides or carbonates from chemical degradation of steels, although this is not explicitly determined.

We consider that study of this material is extremely important and highly relevant to consideration of the behavior of dusts during decommissioning, since such a mixture is clearly typical of what might be encountered in practice – at least from a Magnox-type reactor.

Particle-size distribution was obtained both as a suspension in air and as an emulsion in liquid following ultrasonic dispersion. A typical granulometry for air dispersion is shown in Figure 4-5:



Media pesata in volume: 26.840 um **Media pesata su superficie:** 8.723 um

0% inferiore a: 4.695 um **50% inferiore a:** 18.683 um **90% inferiore a:** 57.132 um

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Size (µm)	Volume in %
0.200	0.00
0.250	0.05
0.312	0.19
0.390	0.27
0.487	0.30
0.608	0.30
0.760	0.29
0.949	

Size (µm)	Volume in %
0.949	0.31
1.185	0.40
1.480	0.59
1.849	0.90
2.309	1.35
2.884	1.91
3.603	2.56
4.500	

Size (µm)	Volume in %
4.500	3.33
5.621	4.25
7.021	5.38
8.770	6.67
10.954	7.99
13.683	9.09
17.091	9.73
21.348	

Size (µm)	Volume in %
21.348	9.69
26.665	8.93
33.306	7.57
41.602	5.92
51.963	4.29
64.906	2.93
81.072	1.93
101.265	

Size (µm)	Volume in %
101.265	1.30
126.487	0.89
157.991	0.55
197.341	0.12
246.493	0.00
307.887	0.00
384.572	0.00
480.357	

Size (µm)	Volume in %
480.357	0.00
600.000	

Figure 4-5
Typical particle-size distribution of material recovered from Latina reactor filtration system

This has a generally smaller particle size than the pulverized unirradiated graphite. The example shown, which is the mean of seven determinations on the same sample, has 10% less than 5.7 µm, 50% less than 30 µm, and 10% greater than 114 µm.

The parametric measurements attempted on this material were:

Minimum ignition temperature

Using the same apparatus as for the unirradiated material, no ignition was possible for concentrations in the range 125 – 350 g.m^{-3}. Although the range of tests was much more limited than that for the unirradiated graphite, SSC classified this irradiated material as *non-flammable*.

4.2.4 Explosion Parameters

Similar tests to those described above for unirradiated graphite powder were conducted on the reactor sample. Under all conditions examined, the material failed to ignite and therefore there are no relevant data. The substance was classified by SSC as *non-explosible*.

4.3 Japan

Work has been conducted in Japan in support of the decommissioning of the Tokai 1 Magnox reactor. In this reactor there is a graphite waste legacy both from the core components (moderator/reflector) and from the graphite fuel sleeves which were utilized in this design.

The work which is outlined below was presented to the authors in March 2006 at the offices of the Japan Atomic Power Company (JAPC) and at the Nuclear Power Engineering Corporation (NUPEC) on two consecutive days. The work was requested by JAPC, the programme was determined by NUPEC, much of the work was sub-contracted to Fuji Electric Systems, and the copyright appears to reside with the Japanese Nuclear Regulatory Ministry METI. A formal Japanese-language NUPEC report on ‘Graphite Waste Handling Techniques’ has now been released to EPRI [31]. This includes and outline of the dust-explosibility work, but NUPEC have advised that more comprehensive data records no longer exist.

The general strategy for Tokai 1 decommissioning was comprehensively presented at the Fourth International Nuclear Graphite Specialists Meeting in Marugame, Japan in September 2003, and was published in the form of a PowerPoint presentation [32]. In essence, it was planned at that time to pursue the goal of incinerating the graphite sleeves. The fate of graphite blocks from the core itself was not yet decided, although incineration is also contemplated, at least for the less-activated portions of the stack. However it is likely in this case that the Japanese regulatory authorities would require separation of ^{14}C from the off gases, and investigations on ^{14}C separation by pressure-swing adsorption and immobilization using the Sabatier process to re-form solid carbon are currently in progress. The pressure-swing adsorption process is expected to be the subject of a further EPRI investigation commencing 2006.

A hard copy of the presentation made to the present authors in Mar 2006 is also available as a reference [33]. This adheres broadly to the 2003 plan, and the presentation covered both solid graphite and graphite dusts, the material in each case originating from archived Tokai blocks (Pechiney graphite). This material utilizes Texas Lockport coke, and the product has irradiation behavior similar to that of UK Pile Grade A: the grades were known as Q_1 (first quality, for moderator, doubly-impregnated) and Q_3 (lower quality, for reflector, single impregnation) [34].

In brief, the work conducted on solid blocks was rather similar to the Italian work already described: direct heating by a plasma torch and a ‘powder-gas’ torch, where no oxidation continued after the torches were removed; and heating of graphite samples in a tubular electric furnace to confirm the criteria identified by Schweitzer (see previous EPRI report for further details on this [1]), these studies including the effects of FeO as a potential catalyst (this material being produced in the powder-gas torch) and also enhanced concentrations of oxygen. The work programme was considered to follow the likely activities taking place in the vicinity of the core graphite components, and the chosen configuration for study was that of a channel, the greatest apparent concern being that of initiating a channel fire analogous to that previously routinely assessed for UK Magnox reactors following a hypothetical air-ingress incident during operation, based upon old computer codes known as RHASD[10] and CFIRE[11]. The effects of hot metal swarf were found to be insignificant, as in the Italian work, and electric sparks were unsurprisingly equally unsuccessful in initiating any oxidation of the solid graphite.

In this work on solid material, the explosion risk was considered to be not at issue. A dust burden of 40 g.m^{-3} (gas volume) has been assessed for the reactor whilst the only potentially ‘dusty’ situation requiring assessment was considered to be the torch cutting operations, where a judgment had been made that the dust concentration will not exceed 490 g.m^{-3}.

On this basis, a programme of deflagration tests was proposed using dusts in the concentration range 10 – 600 g.m^{-3}.

Initial tests utilized a Hartmann bomb apparatus of 30 litre capacity, and a 10 J spark as ignition source. A fine particle distribution described as $< 25\ \mu$m was employed, although no information about this measurement is available. These tests also employed enhanced oxygen concentrations, up to 55% by volume.

As no explosions were initiated, the concentration of powder was greatly increased in a step-wise fashion to a maximum of 7000 g.m^{-3} (tested at 35% oxygen). The concentration range 2000 – 6000 g.m^{-3} was tested at 45% oxygen, and up to 5000

g.m^{-3} at 50% and 55% oxygen, the latter concentration seeing the full range of concentrations down to below 600 g.m^{-3}. In no case was a deflagration observed.

In devising these tests, little account seems to have been taken of the ability of high concentrations of any dust to cause the extinguishing of any potential deflagration through the provision of a large mass of solid material acting as a heat sink. However, the use of high oxygen concentrations is interesting in that it extends the data (and the comforting result of ‘no explosion’) in this direction in a comprehensive fashion: only the UK has additionally considered super-atmospheric oxygen concentrations (Section 4.4.1) and they were not investigated in a systematic fashion.

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[10] **R**eactor **H**eating **A**fter **S**hut**D**own

[11] **C**hannel **FIRE** (propagation assessment)

The failure to initiate any deflagration with 10 J led to a decision to use much higher energy igniters. Tests were conducted up to 10 kJ with both ‘fine powder’ (<25 μm) ands ‘coarse powder’ (< 300 μm) in a 30-litre vessel. A matrix of results (shown below) appeared to identify a critical concentration (in either case) of approximately 250 g.m^{-3} above which no explosion was achieved in either case up to 8 kJ ignition energy: a rather vaguely defined “explosion” area was defined lying below this concentration and above 2 kJ ignition energy (Figure 4-6):

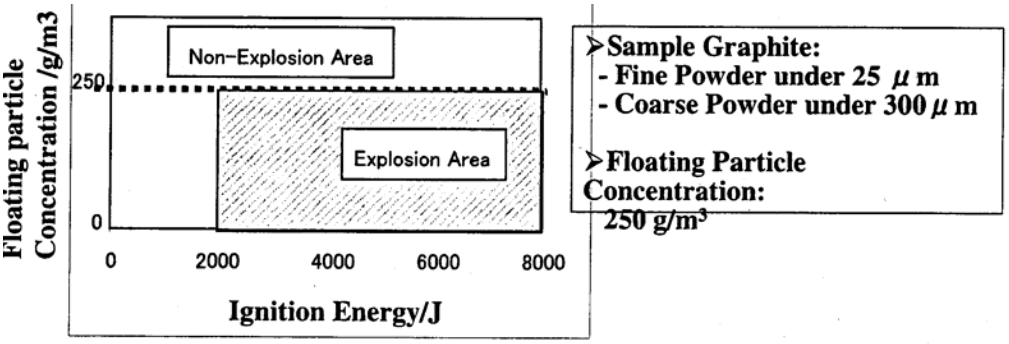

Figure 4-6
Fuji Electric Systems Data on Boundaries for Explosibility of Pechiney Graphite Dust

Underwriting this diagram in the Japanese-language report [31] is a matrix of experimental work with a deflagration indicated by a filled circle and ‘no deflagration’ by a cross. We also observed an additional graph during discussions in Japan, which cannot be reproduced here[12], which confirms positive results for a deflagration with 400 and 600 g.m^{-3} concentration (but not at 300 g.m^{-3}) with 2.5 kJ ignition energy and an oxygen concentration of 17% (but not with 16%), and a further positive result at 300 g.m^{-3} and 2.5 kJ with 18% oxygen. It is assumed that these concentrations refer to additional oxygen above atmospheric, since otherwise the non-explosion area alleged in Figure 4-6 would make no sense. The threshold between deflagration and no deflagration appears to be leveling off at around 250 g.m^{-3} concentration for increasing oxygen concentrations towards (and exceeding) atmospheric concentration, for the 2.5 kJ igniter.

A further graph examined from the Japanese data explains in more detail the differences in behavior between ‘coarse’ and ‘fine’ powder as cited in the legend of Figure 4-6. In fact, four separate powders were studied, being the ‘coarse’ and ‘fine’ components of both moderator-grade (Q_1) and reflector-grade (Q_3) Pechiney material, and their behavior was very slightly different between grades. Each of the four samples was studied as a function of ignition energy, with the following thresholds for a deflagration identified:

coarse powder (<300 μm), reflector grade Q_3:	deflagration at 5 kJ and higher *(one test out of two ignited at 4 kJ)*
coarse powder (<300 μm), moderator grade Q_1:	deflagration at 5 kJ and higher
fine powder (<25 μm), reflector grade Q_3:	deflagration at 2 kJ and higher

---

[12] NUPEC advises that the supporting documentation for this work is now no longer available.

fine powder (<25 μm), moderator grade Q_1: deflagration at 2 kJ and higher

In each case, use of an igniter energy 1 kJ lower than the threshold gave a negative result three times.

These results demonstrate that the finer particles are more able to participate in flame propagation without self extinguishing. The slightly lower purity of the reflector grade may account for the slightly lower apparent threshold for its ignition with the coarse powder, but there are insufficient data for this to be certain.

Whilst it should have been possible to obtain useful data on explosion parameters (max explosion pressure, maximum rate of rise, and K_{st} using the Hartmann-style apparatus, no such data seem to be available. NUPEC and Fuji have however undertaken some work jointly on modeling the deflagration progress in graphite dust based upon the classical understanding of graphite oxidation kinetics.

The Japanese report also includes information about the effects of two additives – iron powder and iron oxide (FeO), these materials being associated with the thermic lance cutting equipment[13]. The following results were obtained:

Effect of Ignition Energy	**1kJ**	**3kJ**	**4kJ**	**5kJ**	**10KJ**
Fe	×	×	√	√	√
FeO (5%)	×	×	√	√	√

Effect of Dust Concentration ($g.m^{-3}$)	**250**	**300**	**400**	**500**	**700**
Fe	×	×	√	√	√
FeO (5%)	×	×	×	√	√

The precise concentration of Fe powder in the graphite dust in these tests is not clear, but it may be assumed to be of order 5% similar to that of the FeO. Particle-size distributions for the additives are also not available.

By comparison with Figure 4-6 we may conclude that both Fe and FeO cause an inerting effect, in that the threshold ignition energy for a deflagration is approximately doubled to 4 kJ. The second table also suggests that FeO is a more effective inerter than Fe, in that the 400 $g.m^{-3}$ concentration did not deflagrate in its presence whereas that with Fe present did. This is consistent with the Fe being readily capable of oxidation whereas FeO is an oxidized form which, although capable of further oxidation to Fe_2O_3 or Fe_3O_4, is much less labile under the

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[13] FeO formation in a thermic-lance environment is probably less likely than Fe_3O_4, formation of which is favoured over Fe_2O_3 above 1400ºC. If sufficiently finely divided, FeO will oxidise spontaneously to Fe_2O_3 in a reaction which can be pyrophoric. Its choice as 'representative' iron oxide in these tests is therefore a little surprising.

conditions of an ignited dust deflagration. Clearly, in this case, both additives are capable of acting as inerters (heat sinks) at the lower ignition energies and dust concentrations.

The final item of work undertaken in Japan involved thermogravimetry on what is described as ‘bandsaw’ powder – graphite dust collecting from cutting graphite into which between zero and 5% of iron oxide powder was mixed. These mixtures were studied at a range of oxygen concentrations to define limits for self-extinguishing and self-sustaining oxidation. The detailed results from this work are not available. However, broadly, it was found that with ambient air (21% oxygen) the oxidation was self extinguishing below approximately 560ºC in air and self sustaining above these temperatures, whereupon the sample would reach temperature several hundred degrees higher (*e.g.* ~1120ºC in ambient air). The effect of additional oxygen was to *reduce* both the ignition temperature and the upper temperature achieved through self-ignition by around 200 - 250ºC with about 55% oxygen compared with the ambient concentration of 21% in air, whilst the effect of larger quantities of impurity was as found in the previous tests – a reduction in reactivity.

It appears that the Japanese work was concluded without the complete resolution of these final experimental results when it was decided that sufficient information was available to indicate that graphite dust offered no explosion risk in the dismantling of the Tokai 1 reactor (and presumably future HTR plant also).

There is however one additional feature of the Tokai 1 reactor which should be mentioned. The operating regime of this plant was unique amongst Magnox reactors in that the carbon-monoxide concentration in the coolant was not controlled at the typical value of 1.0 – 1.5% (as in the UK, Italy and France) but rather was allowed to reach an equilibrium concentration between maintenance periods which was often of order 4%. This resulted in a propensity towards the radiolytic deposition of amorphous carbons which initially was controlled by a relatively high hydrogen concentration, the mechanism of which was evaluated through UK work and published in early 1985 [35]. At almost the same time, strenuous efforts were being made in all Magnox reactors to reduce the hydrogenous impurities in the coolant in order to protect mild-steel components from oxidation. In Tokai 1 this reduction was particularly successful but, in consequence, the protection against carbon deposition was lost, and a problem of copious carbon deposition resulted, most noticeable upon fuel elements in the lower part of fuel channels and sufficient in certain cases to almost completely infill the gas space between the metallic fuel element and the surrounding graphite sleeve.

A related problem, but on a smaller scale, occurred in the UK Hinkley Point ‘A’ reactors which always had a particularly low hydrogenous burden in the coolant because air bearings were used in the gas circulators rather than oil bearings (the usual source of hydrogenous content).

One of the present authors (AJW) was closely involved in the resolution of this problem at Tokai 1 through the application of oxygen injections followed by a modification to the coolant-chemistry regime, and it is extremely unlikely that any significant quantities of this dust (which would be more reactive to air than general graphite dusts) now remain above the background found in all Magnox reactors. Observations in the UK reactors at Berkeley and Hinkley Point ‘A’, where such oxygen injections were also carried out, confirmed effectively 100% removal of all loose and most of the adherent material. The deposits are associated with graphite surfaces and maximized in the cooler half of the reactor stack, but are also found in boiler units associated with particular steels and within certain ranges of tube temperature. The possibility of finding residual reactive carbonaceous material as dusts in these areas during reactor decommissioning should therefore be borne in mind.

4.4 United Kingdom

4.4.1 Experimental Work Commissioned by UKAEA in Support of WAGR Decommissioning

It is useful to begin much earlier than the WAGR decommissioning project, with the Dust-Suspension Reactor Concept [36] as this is probably the earliest consideration of the dust-deflagration problem in the UK. The objective of the concept study was to 'improve' the Magnox-reactor concept by increasing its efficiency of heat removal, using a much denser coolant consisting of carbon dioxide and graphite dust. In the course of this somewhat bizarre concept, attention was rightly paid to the possibility of a dust deflagration in the event of air gaining access to the hot coolant. Experiments were conducted with two commercially available graphites, one being known as 'Foliac' powder.

The particle-size distribution in the powdered material was determined by Andreasen analysis at Morgan Crucible Ltd for one graphite, and by Coulter Electronic Ltd for the second. In the first case, 97% of the material was found to be < 8.4μm and approximately 50% to be below about 4.5 μm; for the second material, 50% was stated to be below 2 μm and approximately 90% < 1 μm.

The samples were placed in a heated steel cylinder to 600ºC and suspended in the air by the shock of an electrical discharge of 4000V, delivering approximately 0.02J. The detection system was a rudimentary pressure gauge.

No explosion was observed with particles greater than 4 μm unless the oxygen concentration in the tube exceeded 90% whilst the powder density was in the range 700 – 1600 $g.m^{-3}$. With powder in the even smaller size range of 1.7 – 2.2 μm the critical oxygen concentration fell to 50% whilst the critical powder density widened to 200 – 2000 $g.m^{-3}$. Much smaller particles were also utilized, and it was found that particles of initially 0.3 μm having been previously exposed to CO_2 at 90ºC would self-heat and inflame upon exposure to air.

In the light of more recent experience in sample preparation within UKAEA and The University of Leeds, these particle sizes appear surprisingly low. Unfortunately the detailed particle-size distributions have not been traced. Not only are these extremely small particle sizes exceedingly difficult to achieve, but sample ageing results in agglomeration to much larger effective sizes within a short time period. No particle remotely approaching these smallest sizes has been found in a reactor circuit, and it is possible that the samples had significantly agglomerated between the time of size analysis and the tests.

'Foliac' powders are clearly not representative of nuclear graphite dusts derived from large components, but in any case the result are most encouraging, except for the sub-micron particles, since oxygen concentrations much higher than in ambient air were needed to initiate any reaction.

This reactor concept was not followed up, and no further attention was paid in the UK to dust deflagration until the decommissioning of the Windscale prototype Advanced Gas-Cooled Reactor (WAGR) was being considered.

At this stage, a number of tests were conducted [37] using representative (but unirradiated) PGA graphite powder with *mean* particle sizes 200 μm and 20 μm. The tests included:

dropping the dust into a 'cherry-red'-hot graphite block;

burning steel immediately above the dust;

dropping the dust on to a red-hot steel plate

plunging a red-hot metal rod into the dust; *and*

flame cutting a mild-steel block containing channels into which graphite dust had been introduced.

Although the burning gas jets in the last activity caused some particles to reach white heat momentarily, no evidence of explosion was found.

Work continued sporadically, with the most likely dust hazard in decommissioning WAGR considered to be ignition from a remote cutting torch gas flame in the presence of possible aluminium and ferrite dusts in the presence of graphite dust in unknown quantities. In 1982 it was confirmed in a crude test using a horizontal tube with a red-hot centre section that coal dust was liable to a deflagration when blown through the tube whereas dust from PGA graphite was not.

It was decided to commission more appropriate tests from the then UK Fire Research Station (FRS), utilizing the 'Swiss' 20-litre spherical vessel [38].

Initial tests at FRS dispensed with the chemical igniters ordinarily utilized in this test at that time, on the basis of FRS advice that the behavior of a substance which was believed to be at worst only weakly explosible would be difficult to determine in the presence of the explosion pressure from the igniters. A 100J capacitative discharge was therefore employed.

Parameters for the test are described in detail, following what had become the standard procedure for the 'Swiss' 20-litre apparatus [39] except for the chemical igniter. The vessel was evacuated to 0.4 bar: the powder reservoir pressurized to 21 bar absolute, and the ignition source activated 60 ms after the dispersion of the dust (upon which the pressure in the vessel was again close to atmospheric). Piezo-electric transducers measure the explosion pressure and its rate of change.

The FRS report does not state the source of the test samples, and a thorough examination of extant correspondence from the period does not identify the exact material either, although it is described as "unirradiated graphite dust supplied by Windscale Nuclear Laboratory[14] *(UKAEA)* made up from a selection of graded particle graphite machinings which gave an approximate representative sample to that removed from the reactor" [40]. It is extremely likely that the

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[14] Now Sellafield (BNFL and UKAEA)

graphite source was Pile Grade 'A' since this was the material employed for the construction of both WAGR and the four early Magnox reactors on the Windscale site, and we know from other work that there is no apparent archive of unirradiated material representing the earlier AGXP graphite used in the Windscale piles.

There were two grades of this sample: 'standard' and 'fines'. Their particle size ranges are tabulated in [38] as follows:

Standard powder:

9.46%	> 180μm
19.56%	125-180 μm
19.56%	90-125 μm[15]
16.77%	63-90 μm
12.29%	45-63 μm
22.36%	< 45 μm

Fines:

2.20%	> 180 μm
10.00%	125-180 μm
15.60%	90-125 μm
20.00%	63-90 μm
17.80%	45-63 μm
34.40%	< 45 μm

It is suspected that this distribution was arrived at by sieving, although this is not stated. The number of significant figures, and their rounding in the case of the 'fines', are presented as in the original document.

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[15] An error occurs in [37] in reporting this data: the present table is considered correct

No ignition occurred at all using the 100J source with a range of dust concentrations between 500 – 8000 g.m^{-3} and, after discussions with UKAEA, FRS agreed to employ *two* 10 kJ igniters to '*ensure'* a positive result from the small remaining quantity of sample. Such a result was indeed obtained and, after allowance for the igniters, the following explosion parameters were reported:

	Dust Concentration g.m^{-3}	**Maximum Explosion Pressure (bar)**	**Maximum Rate of Pressure Rise (bar.s^{-1})**	**K_{st} (bar.m.s^{-1}) *(calculated bythe present authors)***
Standard Powder	500	4.14	147	*39.9*
Fines	500	3.82	157	*42.6*

These values are slightly higher than the Italian data, but we reserve further comment on comparisons until Section 5.

Having obtained this result, the work at FRS was terminated by UKAEA, on the basis that the concentrations were 'excessive' (there appears to have been no understanding of the concept of upper and lower explosion limits in selecting test concentrations) and that 'no dusts had been found in the WAGR circuit'. Concern was also expressed subsequently about the 'excessive' ignition energy used to obtain a positive result.

With some feedback from the work initiated in connection with decommissioning the Windscale Piles (discussed in the next sub-section), we can note here that the above arguments, together with some issues about inerters and an analysis of the engineering factors likely to initiate or to contribute to a dust-deflagration incident, were sufficient to create a peer-reviewed safety case which was accepted by the UK Nuclear Safety authorities for the cutting of metallic components above the WAGR core and for the subsequent dismantling of the graphite stack itself. The engineering issues, covering such matters as the creation of ignition sources, adventitious flammable mixtures of gas or powder, etc., are discussed in Section 5. In this *experimental* Section, it is appropriate to move on to the work supporting the decommissioning of the Windscale Piles.

4.4.2 Experimental Work in Support of Decommissioning the Windscale Piles

4.4.2.1 General Description of Reactors and Conditions

The UK had four air-cooled graphite reactors constructed (initially) essentially for military purposes. The oldest of these, the **G**raphite **L**ow **E**nergy **E**xperimental **P**ile (GLEEP) has recently been hand-dismantled after a very low total irradiation. The second reactor, the **B**ritish **E**xperimental **P**ile Zero-Energy (BEPO) remains intact within a concrete shield except for a test coring some four inches in diameter through the shield into the centre of the reactor, to enable isometric assays and other analyses to be made. Two further large production piles were constructed at Windscale, but were closed after the major fire in Pile No. 1 in 1957. These reactors have been mothballed since that time, although a significant amount of preparatory analysis of graphite and other structures has been completed on both piles over the last ten years.

The two production piles are nominally identical, consisting of stacks of AGXP graphite with horizontal fuel and isotope channels through which air was blown to remove heat from the pile. This once-through air flow was discharged *via* a chimney stack and filtration system. Pile 2 is essentially de-fuelled, but in Pile 1 a significant mass of burned fuel and debris remains which blocks numerous channels in the so-called 'fire-affected zone' (FAZ).

The piles were operated with the graphite at temperatures in the range 30 - 130ºC and therefore much of the graphite still contains a significant Wigner energy content. The dust burden is generally low away from the FAZ of Pile 1, although sample analysis has confirmed the presence of particles originating from the concrete air ducts within the graphite pores. As may be imagined, planning the decommissioning of Pile 1 has occasioned a great deal of debate. A lengthy discussion of the accident and its implications with respect to the behavior of the graphite will be found in [1] and [41].

In the context of dust deflagration considerations, the piles offer a number of unique considerations:

> the presence of Wigner energy within the graphite *(as previously noted)*: this internal energy content potentially makes it easier to combust;
>
> visible evidence of quantities of dust in the FAZ region which may contain materials other than graphite;
>
> the possible presence of a unique ignition source in the form of pyrophoric uranium hydride, resulting from the use of water in the later stages of the fire *(this has subsequently been virtually discounted by careful reconsideration of the chemistry underlying reported* UH_3 *hazards in the nuclear industries of the UK and USA)*;
>
> the presence of potential catalysts arising from combustion products of fuel and isotope cartridges; *and*
>
> the possibly unique *consequences* of a deflagration in terms of the potential spreading of fuel debris and the release of radioactivity to reactor personnel and to the environment: this includes a supposed[16] void space within the FAZ where a deflagration could be initiated which could cause disruption to the core and perhaps lead to a secondary explosion in another region of the containment.

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[16] Recent work on the evaluation of the available oxygen during the event and the consequent mode of graphite loss lead to a view that there is *no* void space [42].

It is therefore unsurprising that additional reassurances were sought on this topic to reinforce the planning of engineering solutions for handling the dismantling of the damaged structure. In addition, the UK regulatory bodies demanded a safety case to cover the consequences of a seismic event in pile 1, requiring assurance that such an event would not mobilize a dust cloud which could result in a deflagration. In fact a specific earthquake of magnitude 5.6 on the Richter scale was specified, consistent with an acceleration of 0.25g, which is predicted to occur on the reactor site with a probability of one in 10,000 years. It is suspected that underlying this requirement was a mistaken impression that the same event could release Wigner energy from the graphite which, in combination with foreign and potentially catalytic materials, would present a significant ignition source.

4.4.2.2 Leeds University Research Program

To provide the independent reassurances, it was decided to use an independent laboratory at The Energy and Resources Research Institute, The University of Leeds, UK. The requirements were very broadly defined initially, without assumptions about the ignition source or reliance on older information, as follows:

> could graphite dust explode?
>
> could the overpressures generated in an initial graphite dust explosion damage the graphite core (assuming that it took place within the FAZ either in the supposed void space of in fuel channels), generating further dust that could lead to a secondary explosion?
>
> could an initial explosion which did not disrupt the core nevertheless escalate through secondary explosions in the connected volumes beyond the fuel channels and perhaps disrupt the reactor charge walls?

To address these broad questions, the following specific test program was agreed:

> determine explosibility of graphite dust and hybrid methane/graphite mixtures in the standard 1 m^3 ISO test rig (the use of methane as a driver with known explosion characteristics was considered certain to be necessary in order to obtain meaningful data on graphite dust alone);
>
> determine flame speeds and temperatures;
>
> determine the ignition characteristics of graphite dust in the Hartmann apparatus;
>
> make a determination of likely overpressures in the reactor geometry in a scaled-down version, using methane;
>
> determine whether a secondary graphite dust explosion was possible in through interlinked volumes approximating to the reactor volume ratios;
>
> determine the extent of burnout of graphite particles passing through a flame front using the CBK8 model;
>
> determine the effect of likely contaminants on the behavior of the graphite dust (the likely contaminants in pile 1 being primarily lead (and oxides) and aluminium (from the fuel); *and, arising from observations during the experimental programme*
>
> quantify approximately the agglomeration of graphite particles with time.

The work programme was devised by UKAEA in discussions with The University of Leeds and specialist members of the Windscale Projects Technical Committee, of which one of the present authors (AJW) is a member. The program was then managed by BNFL, who arranged for the graphite supply. Since no AGXP representative of the piles graphite was available, a consensus was reached that Pile Grade 'A' archived from the Calder Magnox reactors was an acceptable substitute.

Obtaining the specified granulometry proved surprisingly difficult. The supplied graphite was in blocks of dimensions 9" x 9" x 12", and these were broken by sledgehammer into small pieces, protecting the graphite first with plastic sheeting. A Retsch ZM100 milling machine was then employed but proved extremely unsatisfactory with the specified sized material, and a jaw crusher had to be used first to reduce the size of the fragments to millimetre-sized grains. The miller was then employed to produce a powder mainly < 60μm, with the first batches being discarded.

Whilst the product included material below 10 μm (the specified upper size limit for the work), the average particle size produced by the Retsch machine was higher than specified with only 19% satisfying the < 10μm criterion. Accordingly, an external contractor was engaged to further grind and separate/classify the material before use in the tests. The result was a powder ground to < 30μm with 80% < 10 μm, although separation was not possible because it was found that the particles rapidly agglomerated. This issue is discussed later. The resulting distribution shows a very strong peak at around 7 μm and is shown in graphical form and as the standard Mastersizer output for comparison with other samples discussed in this review:

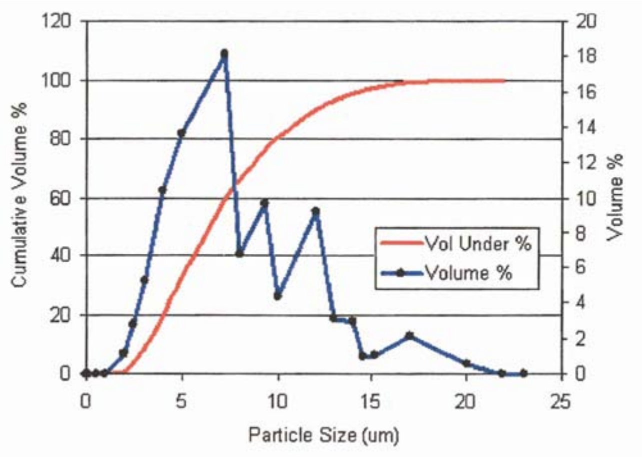
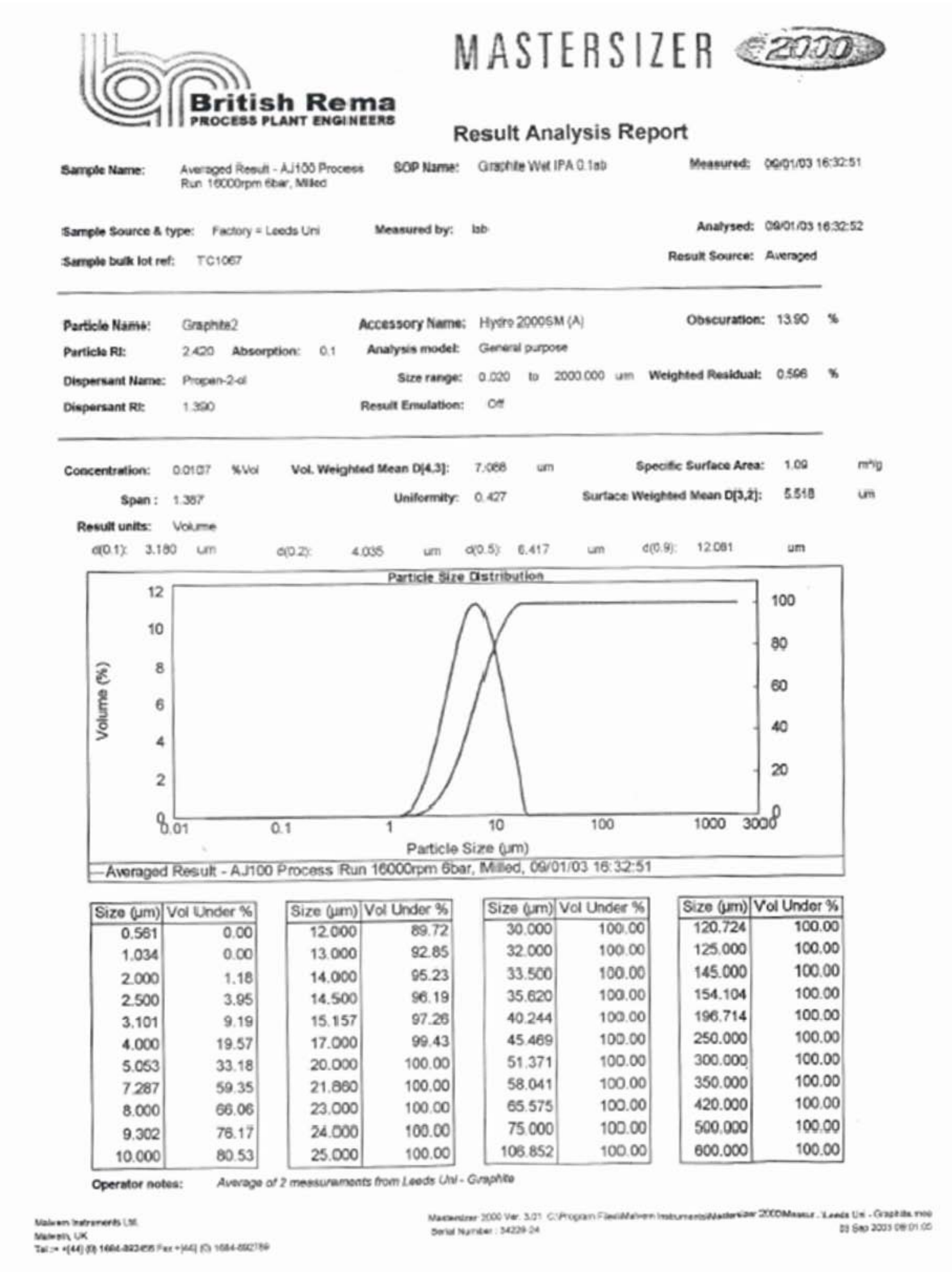


Figure 4-7
Size Distribution of PGA Graphite Dust Used at The University of Leeds, UK



British Rema
PROCESS PLANT ENGINEERS

MASTERSIZER 2000

Result Analysis Report

Sample Name: Averaged Result - AJ100 Process Run 16000rpm 6bar, Milled
SOP Name: Graphite Wet IPA 0.1ab
Measured: 09/01/03 16:32:51

Sample Source & type: Factory = Leeds Uni
Measured by: lab
Analysed: 09/01/03 16:32:52

Sample bulk lot ref: TC1067
Result Source: Averaged

Particle Name: Graphite2
Accessory Name: Hydro 2000SM (A)
Obscuration: 13.90 %

Particle RI: 2.420 **Absorption:** 0.1
Analysis model: General purpose

Dispersant Name: Propan-2-ol
Size range: 0.020 to 2000.000 um
Weighted Residual: 0.596 %

Dispersant RI: 1.390
Result Emulation: Off

Concentration: 0.0107 %Vol
Vol. Weighted Mean D[4,3]: 7.068 um
Specific Surface Area: 1.09 m²/g

Span : 1.387
Uniformity: 0.427
Surface Weighted Mean D[3,2]: 5.518 um

Result units: Volume

d(0.1): 3.180 um d(0.2): 4.035 um d(0.5): 6.417 um d(0.9): 12.081 um

Size (µm)	Vol Under %
0.561	0.00
1.034	0.00
2.000	1.18
2.500	3.95
3.101	9.19
4.000	19.57
5.053	33.18
7.287	59.35
8.000	66.06
9.302	76.17
10.000	80.53

Size (µm)	Vol Under %
12.000	89.72
13.000	92.85
14.000	95.23
14.500	96.19
15.157	97.26
17.000	99.43
20.000	100.00
21.860	100.00
23.000	100.00
24.000	100.00
25.000	100.00

Size (µm)	Vol Under %
30.000	100.00
32.000	100.00
33.500	100.00
35.620	100.00
40.244	100.00
45.469	100.00
51.371	100.00
58.041	100.00
65.575	100.00
75.000	100.00
106.852	100.00

Size (µm)	Vol Under %
120.724	100.00
125.000	100.00
145.000	100.00
154.104	100.00
196.714	100.00
250.000	100.00
300.000	100.00
350.000	100.00
420.000	100.00
500.000	100.00
600.000	100.00

Operator notes: *Average of 2 measurements from Leeds Uni - Graphite*

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.01
Serial Number : 34229-24
03 Sep 2003 09:01:05

Figure 4-8
Size distribution of PGA graphite dust used at The University of Leeds, UK Mastersizer 2000 report on particle size distribution of PGA graphite used at The University of Leeds, UK

This is a *very* much finer dust than employed in the Italian studies, for example.

4.4.2.3 Hartmann Apparatus

A very limited number of tests were conducted with the Hartmann apparatus using a continuous arc of energy 4J. The apparatus was proven with maize flour as the standard calibration material, for which deflagrations were obtained at concentrations above about 200 g.m^{-3}. These continued up to the maximum tested, 827 g.m^{-3}.

For graphite there was no reaction at any concentration between 42 and 1001 g.m^{-3} except that the conducting nature of the particles allowed some bridging of the arc, with small sparks developing. Drying the sample overnight made no difference with the 500 g.m^{-3} sample tested.

4.4.2.4 ISO Rig Test Data

The Leeds vessel (shown in Figure 3-3) is constructed to the general specifications of the ISO standard [21] but with some small deviations (which the standard permits) in order to facilitate the rapid turnaround of tests. The vessel volume is slightly oversize, at 1.138 m^3, the external chamber is 4.5 litres and connected to the perforated C-ring within the vessel *via* a fast-acting pneumatic ball valve. The dust pot is initially pressurized to 20 bar and the main vessel pressure reduced to 923 mbar. Where a methane driver was employed, the methane was added to the main vessel volume using the technique of partial pressures. The ignition delay was 0.6 seconds to ensure that all dust had entered the vessel. Chemical igniters of energy between 5 and 15 kJ were mainly used, firing into a small hemispherical cup in the centre of the vessel to limit any problems resulting from directional ignition. A small number of later tests were conducted using igniters of 1 kJ, 2kJ, 3kJ and 4kJ. These confirmed that the threshold energy for initiating a deflagration in the graphite alone lay around 4 – 5 kJ.

Thermocouples are present at fixed positions within the vessel to allow measurements of flame speed and temperature, and there is full piezoelectric pressure instrumentation.

Figures 4-9 and 4-10 illustrate respectively the timescale of pressure changes within the vessel for a typical experimental run, and the relationship between maximum pressure attained and chemical igniter energy, which must be allowed for in evaluating the explosion parameters of the dusts:

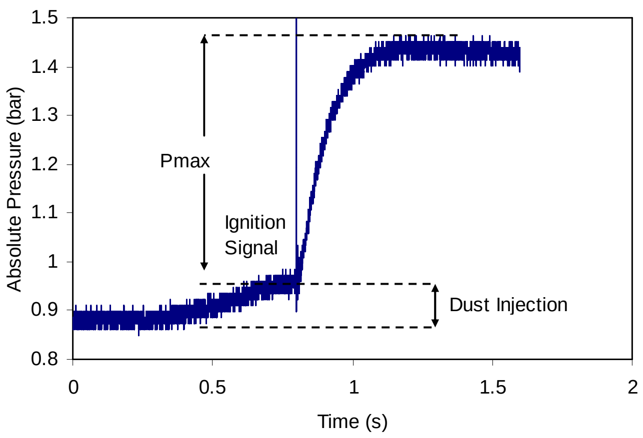


Figure 4-9
Pressure/Time Relationship for a Typical Deflagration in the Leeds Apparatus

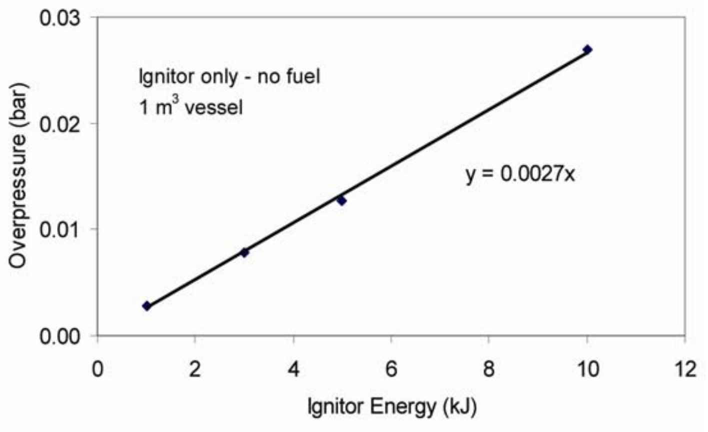


Figure 4-10
Overpressure as a Function of Igniter Energy

Following the negative results obtained in the Hartmann apparatus, there was concern that meaningful results could be obtained with graphite alone in the ISO rig. It was decided to conduct a lengthy series of tests were conducted using graphite in the presence of a methane ‘driver’, methane alone, and maize flour, before proceeding to tests with graphite alone. The full sequence of tests in the first phase of the work is listed in *Appendix B*.

The logic of this apparently complex approach to the problem is that graphite alone is clearly so weakly explosible that the pressure pulse and the apparent explosion parameters are completely dominated by the behavior of the chemical igniters and, in consequence, any data obtained are subject to significant uncertainties. In addition, the initial observations quickly established that, with the particular granulometry of dust used, a significant proportion remained unburned. In their first report to BNFL on behalf of UKAEA [43][17], the Leeds authors describe a sophisticated

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[17] This report was independently peer reviewed [44] by a person with 25 years’ experience in the gas and dust explosion field, whose comments were included.

methodology to evaluate the independent behavior of the graphite, deconvoluting the data from the effects of the chemical igniters by utilizing 6% methane in the air within the vessel to provide a larger, more measurable effect since the lean methane/air mixture acts as a large flame front ignition source. The behavior of 6% methane in the absence of graphite was readily established with identical chemical detonators being used, and this in principle would allow the characteristics of the graphite to be established.

However, two other issues needed to be addressed. Firstly, this is not a standard methodology in the ISO specification, and so it was decided to validate the 'methane-driver' technique independently using maize flour, the standard high-reactivity material utilized in the industry for the calibration of test systems. To conform as closely as possible to the ISO specification, the maize was sieved to < 70 μm, the normal requirement for dust-explosibility tests if specific particle sizes are not being addressed. An additional complication in the presence of methane is that the great majority, if not all, of the graphite participates in the deflagration because of the higher energy input available from the burning methane. An essential requirement before the analysis is fully complete is therefore to collect the residues from one or more methane-driven tests and assess the mass consumed and (ideally) the particle-size distribution of the residues.

It may also be noted that in tests involving methane/maize and maize alone, the maximum overpressures reached were similar for the optimum concentration of the maize dust indicating that the available oxygen was all consumed. The key data from tests involving maize, which are needed to interpret the graphite data, are given in the following table:

	6% CH_4 Only	**Maize Only**	**6% CH_4 + Maize**	**Graphite Only**	**6% CH_4 + Graphite**
K_{st} (bar.m.s^{-1})	120	160 (@ 550 g.m^{-3})	330 (@ 350 g.m^{-3} maize or 395 g.m^{-3} total flammable content)	14	200
P_{max} (bar)	6.1	8.5 (@ 700 g.m^{-3})	8.4 (@ 264 g.m^{-3} maize or 309 g.m^{-3} total flammable content	0.5	7.7

The ratio of the concentrations at which the equivalent peak values of explosion pressure occur for maize and maize plus methane can be applied to the results for graphite. A ratio is also calculable from the values of K_{st}. The concentrations are all above the stoichiometric concentration for maize (220 g.m^{-3}), indicating that even with this material, the largest particles are not fully burning out in the deflagration.

The interpretation of the hybrid tests works on the premise that the ratio of K_{st} values of methane and methane/maize will also apply to graphite: however there is some evidence that this ratio varies with K_{st}, increasing as K_{st} falls [45]. There is also some variability with gas concentration, which was however not varied in this series of tests. This could have been addressed to some extent by carrying out further tests with different concentrations of methane in air, but it was decided that the tests with graphite would proceed directly.

When 6% methane was combined with graphite, the behavior was similar to that observed with maize, as shown in Figure 4-11:

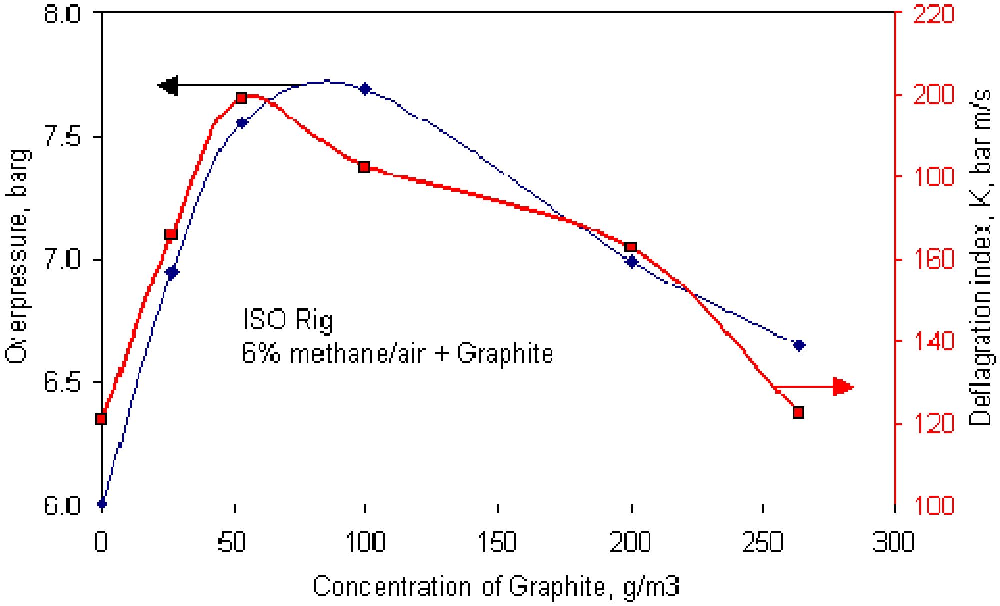


Figure 4-11
Maximum overpressure and deflagration index as a function of graphite concentration in graphite/6% methane studies

The maximum pressure attained was 7.7 bar, 0.65 bar below that attained with the maize/methane mixture. The concentration at this maximum was 105 $g.m^{-3}$, close to the stoichiometric value for graphite alone but much richer than the stoichiometric value for graphite plus methane. The most likely explanation for the lower peak pressure is a lower flame temperature for carbon, possibly due to a greater proportion of the graphite dust not participating in the deflagration than for maize, although the temperatures attained in the two tests were different and this also contributes.

There is a ‘rule of thumb’ for estimating the flame temperature: the ratio of the peak absolute pressure to the initial absolute pressure, multiplied by the initial temperature in Kelvin is close to the peak flame temperature. This gives estimated peak flame temperatures of 2009K for methane/air, 2686K for methane/air/maize, 2727K for maize without methane, and 2497K for methane/air/graphite, assuming a reactant to product mole ratio of unity (which is precisely valid only if the ratio of post-reaction CO/CO_2 is the same in each case). The significance of these estimates is the estimate of an increase in flame temperature (above methane/air alone) due to graphite of 488K and due to maize of 677K. Making one further assumption, that the ratio of pressure and temperature rises due to maize and graphite will be proportional to their peak pressure and temperature ratios under deflagration conditions with no methane present, then one derives a peak pressure for graphite *alone* of 5.7 bar and a maximum flame temperature of 1931K. This is a significant lower value than for maize or typical hydrocarbons and is a principal reason why the deflagration in graphite is poor.

Another measure of reactivity is the flame speed, as determined from the thermocouples present within the ISO vessel. The average flame speeds in the centre of the vessel – between 20% - 80% of the radius and therefore isolated from any effects of the wall or ignition system – are shown in Figure 4-12 as a function of the graphite concentration:

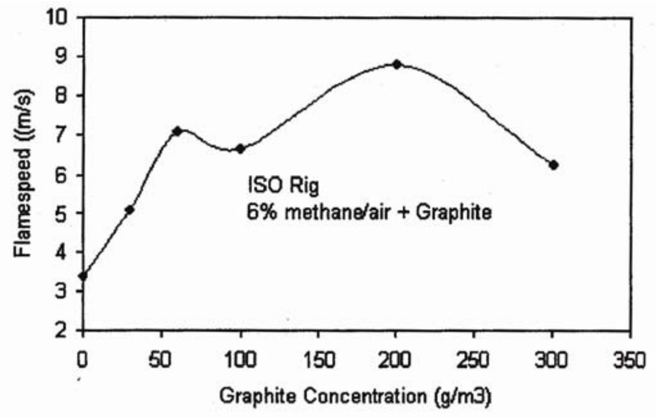


Figure 4-12
Average Flame Speeds in Hybrid Graphite/Methane/Air Mixtures

The presence of the graphite powder results in an almost three-fold increase in flame speed and suggests a maximum flame speed for graphite alone under the ISO conditions of 5.6 m.s-1. The curve displays two peaks, and the first one, at around 55 g.m-3, corresponds with the concentration at which the peak value of Kst was found. The authors of [43] were not able to explain the second peak.

On the basis of these assorted tests with hybrid mixtures and maize, the following results for graphite alone were predicted:

a maximum K_{st} of 61 bar.m.s^{-1} at 86 g.m^{-3};

a maximum peak pressure of 5.7 bar at a concentration of 278 g.m^{-3}; *and*

a maximum constant volume flame temperature of 1931K.

However, the flame speed results with their second peak suggest a different maximum reactive mixture (313 g.m^{-1}) and, since in these tests all of the graphite was consumed whereas it was suspected that different behavior would be found with graphite alone, the programme was moved on to tests with graphite alone.

In this situation, unsurprisingly, the severity of the deflagration was dramatically reduced. Fig 4-13 shows the maximum overpressures as a function of concentration of graphite, and they do not exceed 0.5 bar:

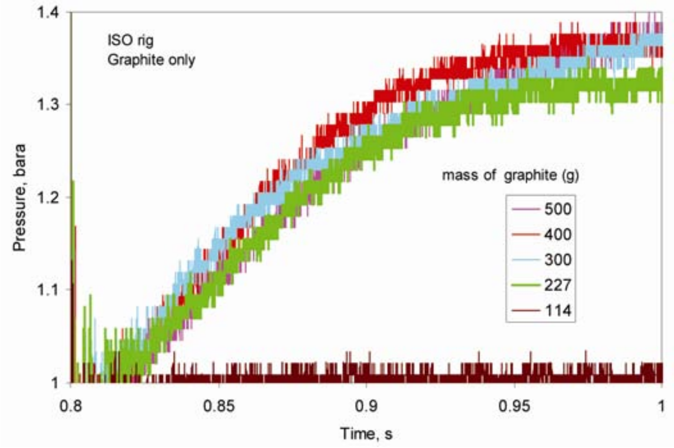


Figure 4-13
Maximum Overpressures for Graphite Alone in the Leeds ISO Apparatus

K_{st} also shows a large reduction compared with the results predicted from the hybrid results:

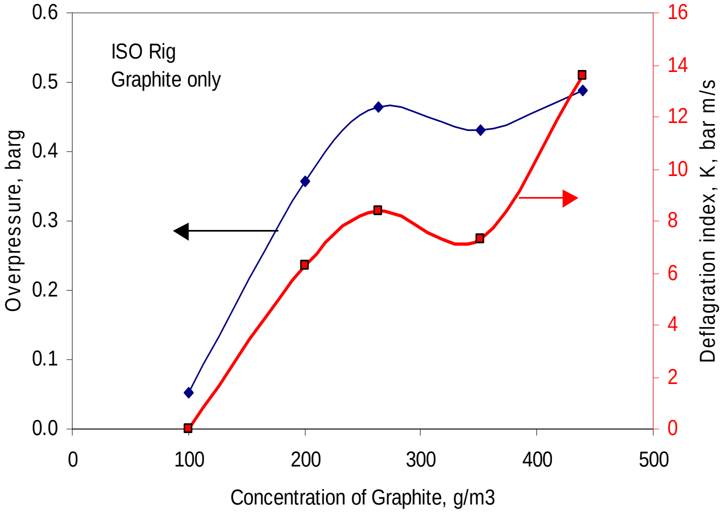


Figure 4-14
K_{st} and Overpressure Data for Graphite Alone in the Leeds ISO Rig

A major difference from the hybrid tests was that as much as 60% of the graphite did not participate in the deflagration. The implication of this is that the 40% which did burn was the finest material, and therefore that less than about 3.5 μm based upon the distribution in Figures 4-7 and 4-8.

There is however an alternative possibility, which is that the flame started to burn around the ignition source but then failed to propagate. This was however resolved by studies of the flame propagation utilizing the thermocouple array in Phase 2 of the Leeds project [46]. Figure 4-15 shows the flame arrival times for the maximum reactivity graphite/air explosion and Figure 4-16 shows the flame speed as a function of distance from the centre of the vessel:

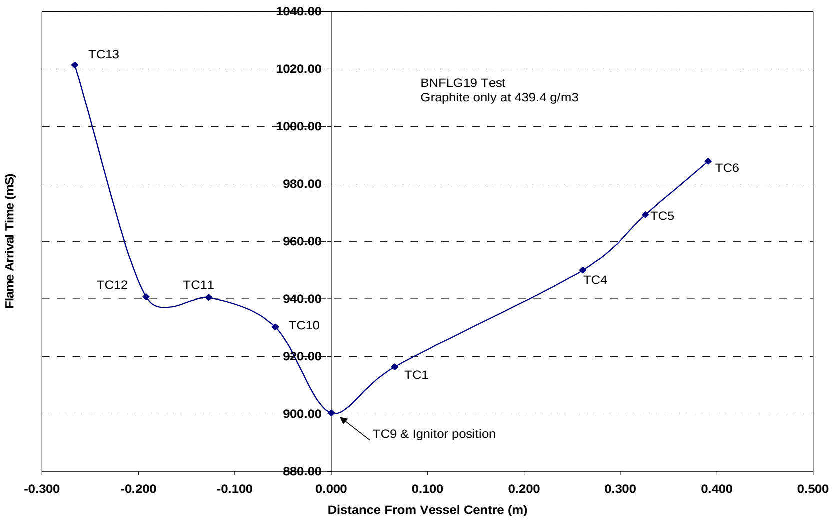


Figure 4-15
Flame Arrival Time for Graphite/Air Deflagration in the Leeds ISO Vessel

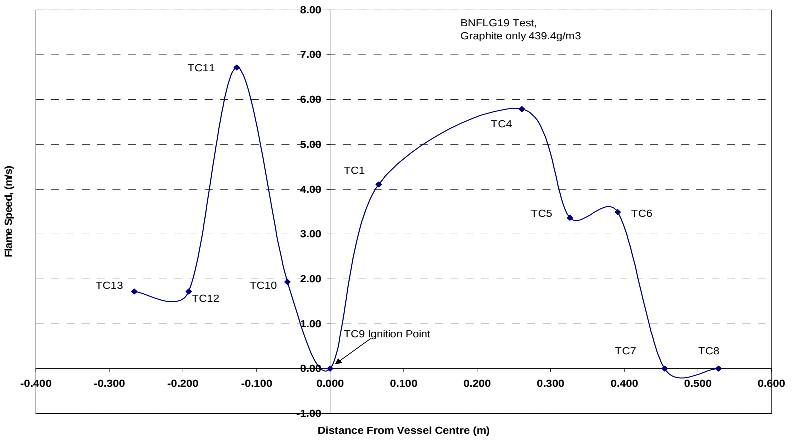


Figure 4-16
Flame Speed for Graphite/Air Deflagration in the Leeds ISO Vessel

The flame arrival records in Figure 4-15 show that the flame spreads to a diameter of at least 0.8m, which is in reasonable agreement with the size deduced from the pressure records. The flame speed records in Figure 4-16 indicate a flame propagation away from the ignition source, that later slows down with a possible identification of flame quenching. This evidence would support the explanation for the low overpressures based on flame quenching at around a 0.9m diameter flame size – in other words, evidence that the flame is self-extinguishing. Ideally, to prove this point, tests would be repeated in larger vessels. However, the French work, to be discussed in Section 4.5, ably demonstrates that this is the case.

There is lengthy debate in [43] and [46] over the question of the unburnt material as to the relative importance of flame quenching and the failure of larger particles to participate in the deflagration. It remains essentially unresolved, but is highly likely that both explanations contribute to the residue of unburnt material and to the consequent low peak pressures. Ref [46] ventures that the maximum particle size which probably participates is 6 μm, but the evidence presented for this particular number is not entirely convincing.

The following is a summary of the ISO rig findings (the original references should be consulted for greater detail):

	Measured Peak (graphite alone)	**Predicted Peak From Methane-Driven Tests**	**Predicted Concentration for Peak ($g.m^{-3}$)**	**Corrected Concentration Assuming 60% Unburnt ($g.m^{-3}$)**	**Measured Concentration for Peak ($g.m^{-3}$)**
K_{st} ($bar.m.s^{-1}$)	14	61	86	215	450
P_{max} (bar)	0.5	5.7	278	695	450
from flame speed tests			313	783	

The apparent wide inconsistency in this table derives largely from the attempts to improve upon the data using indirect means such as the methane driver. Whilst these efforts are to be commended, it is important to record explicitly the following conclusions:

PGA graphite dust was weakly explosible with ignition energies of 5 kJ or higher;

the graphite alone produced a very low maximum overpressure and K_{st};

the flame front appears to be self-extinguishing within the volume of the vessel; *and*

only around 40% of the sample participated in the weak deflagration, and the inference is that this was the finest material, < 6 μm.

4.4.2.5 Tests Specific to Windscale Pile 1

These results are of minor interest in the present context but are mentioned for completeness. A fully instrument approximate scale model of the connected volumes present in the reactor was constructed in order to assess the effects of overpressures and secondary explosions. These tests were *not* conducted with graphite because of its poor explosibility, but with quiescent methane/air mixtures in the range 6 – 10% methane backed up by initial quiescent tests in the ISO rig. The initiating event was established in an enclosure representing a theoretical void within the graphite core, and it was concluded that external structures would be unlikely to be subjected to an overpressure exceeding 0.2 bar.

Secondary explosions were assessed in the same linked geometry using 10% methane/air in the initiating chamber and either 0 or 5% in the rest of the geometry, with graphite powder laid in the linking pipe (representing a fuel channel within the graphite stack. These conditions were chosen as a ‘worst-case scenario’ in terms of induced velocities in the ‘channels’ and maximum turbulence.

The results showed no evidence of any secondary explosion – indeed the overpressures were *lowered* compared with the initial tests, showing that the induced graphite dust cloud behaved as a heat sink thereby partially suppressing the gas explosion in the initiating chamber.

Two issues were identified by the Leeds team which need to be borne in mind:

> the initiating gas explosion may have been over-driven, resulting in excessive turbulence which can result in flame quenching; *and*
>
> the results may be influenced by agglomeration of the graphite powder (discussed in the following sub-section), whereas the agglomeration forces may have been overcome in the ISO test conditions. However, the agglomerated material is likely to be more characteristic of the reactor environment.

In general terms these are very encouraging results, albeit tempered by the somewhat artificial conditions employed.

4.4.2.6 Agglomeration and ‘Ageing’ of Samples

The phenomenon of agglomeration of particles, is illustrated through an apparent problem of repeatability/reproducibility is illustrated in Fig. 4-17 where the overpressure is plotted as function of concentration. Although a consistent and expected trend is shown in terms of “single shot” tests at changing concentration, repeat tests at the same concentration (440 $g.m^{-2}$) – identified as subset A in Fig. 4-17 - show an apparently unacceptable variability. The tests in subset A were conducted under nominally “identical” conditions all using the same 5litre dust pot, same ignition source etc. The main difference between the tests is that they were carried out at different times over a 40 week period.

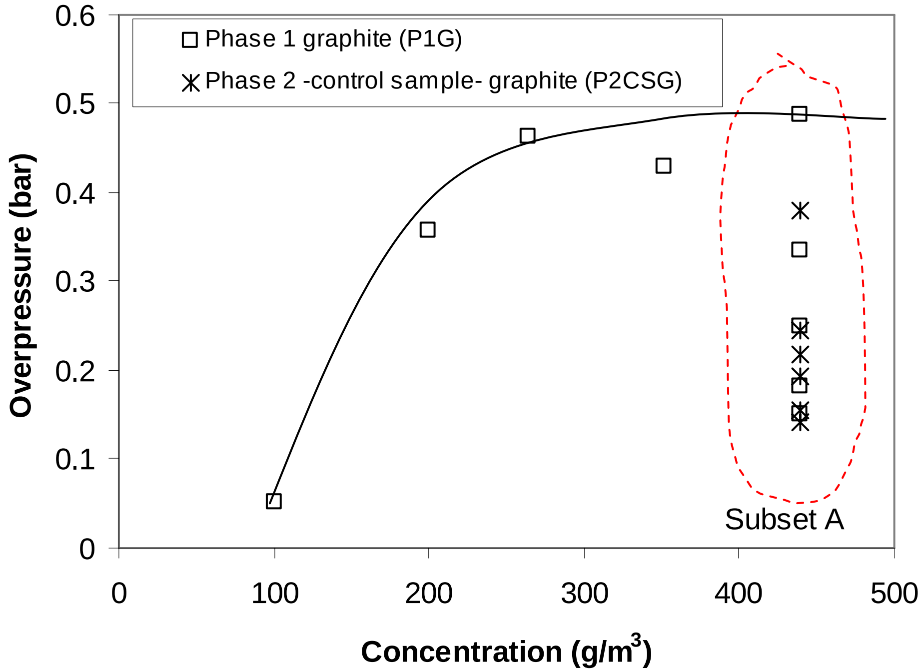


Figure 4-17
Systematic reduction in overpressure with time since preparation of sample, illustrated for two different samples over an interval of 40 weeks at otherwise identical conditions

The supposition that the reduced overpressures arise because the smallest particles are no longer present is supported theoretically by a comprehensive mathematical treatment due to McDuff [47], which examines the energy of particle-particle interactions and concludes that it increases as the separation between the particles decreases. All adjacent particles have a van der Waals attraction which is brought about by a variety of forces, the principal of these being the interaction of dipoles of neighboring atoms and molecules modeled by a Lennard-Jones potential. When the separation distance is comparable to the particle radius, the particle-particle attraction increases as the inverse of the sixth power of the separation; when the radius of particles is significantly larger than their separation distance then the energy of interaction increases with compaction by approximately the square of the distance between particle edges, as verified experimentally by Rioux *et al.* in [48], albeit on different materials. At *very* close approach, the Born repulsion of adjacent electron clouds becomes significant so that, in the absence of other influences, there is an energy minimum at an approach distance of approximately 1 nm.

At this point the question can be asked as to what has happened to the milled graphite dust during storage and drop-handling under normal gravity. If inter-particle separation were gradually decreasing by bulk weight and by compaction during drop-handling, and perhaps by slow particle migration processes, then particle-particle forces must be increasing with time contributing to, or in fact causing, particle ageing. It was shown that the dust-pot injection pressure necessary to achieve the same overpressure in the ISO vessel increased with the age of the sample, other parameters being approximately constant. Rioux *et al.* claim that many aggregates are of fractal nature. This means that where particle size growth is in unit fractal units the particles can grow relatively fast with complex fractal geometries. The fractal geometry of graphite dust was not investigated in the Leeds work, but the re-characterization of the particle-size distribution has subsequently confirmed that the proportion of small (< 5μm) particles is reduced whilst there is a modest increase in those in the 15 – 20 μm range upon storage.

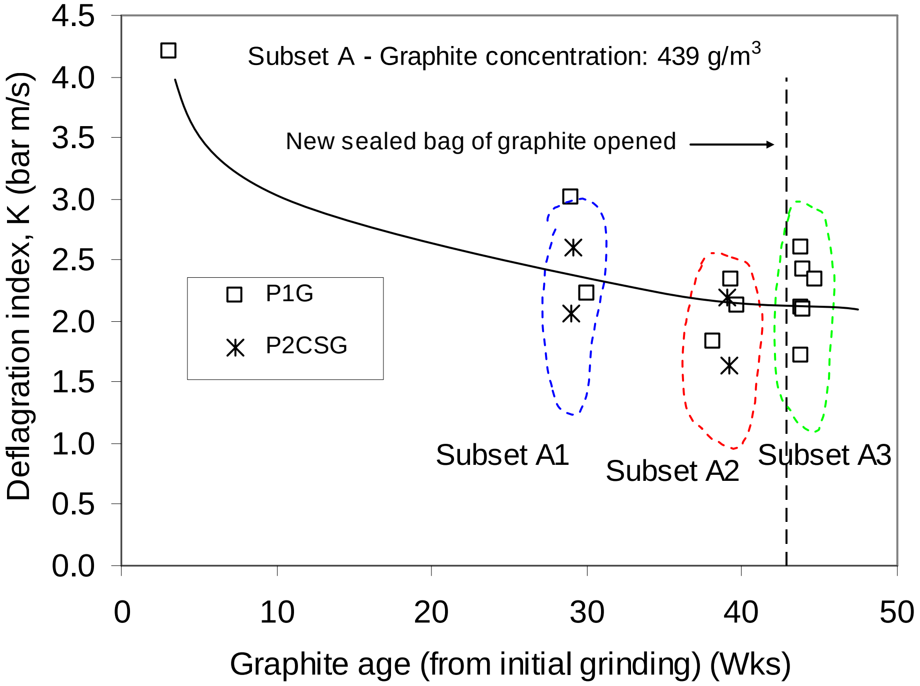


Figure 4-18
Confirmation of the Ageing Effect Upon Deflagration Index, With Additional Aged Samples

The problem with an explanation of a particle ageing effect being due to agglomeration of particles is that the ISO type vessel injection method uses high velocities in the jet air flow of the dust dispersion ‘C’ ring. It is considered by the Leeds team to be unlikely that the shear forces involved in this do not break up any agglomerated particles, unless the agglomerates are very firmly bound together. However, the size-distribution technique that is used is an aerodynamic sizer and the shear forces in this may also break weak agglomerates. Without a laser based in-situ particle size measurement it is very difficult to prove that the particle size distribution in the tested dust clouds is changing with age.

We may however conclude from this that, experimentally, the reduction in both overpressure and deflagration index with sample ageing is real and highly significant, since this will almost certainly apply to any samples encountered in decommissioning of graphite-moderated reactors.

4.4.2.7 The Effects of Additives

Because of the unique situation in Windscale Pile No. 1, the chosen impurities for this study were lead oxide and aluminium oxide, arising respectively from the melting, oxidation and possible dispersion of metallic lead used as spacing components, and from fuel-cladding debris created in the fire. Lead was employed as Pb_3O_4 in this study.

Seven tests were performed with graphite powder contaminated with lead oxide powder at a concentration of 1000 ppm lead (by mass) intimately mixed by opposed jet milling. The results are shown in Figs. 4-19 and 4-20. Lead oxide appears to have no effect on the overpressure and reactivity K compared with graphite alone, as the results lie within the scatter of the results for pure graphite explosions at a particular age.

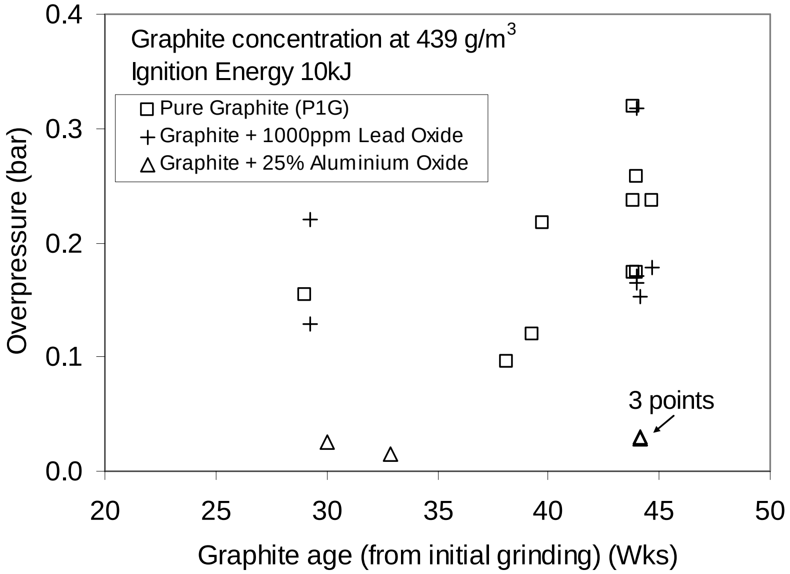


Figure 4-19
Illustrating the lack of effect of catalysts on the overpressure in the ISO Test, in combination with the ageing effect

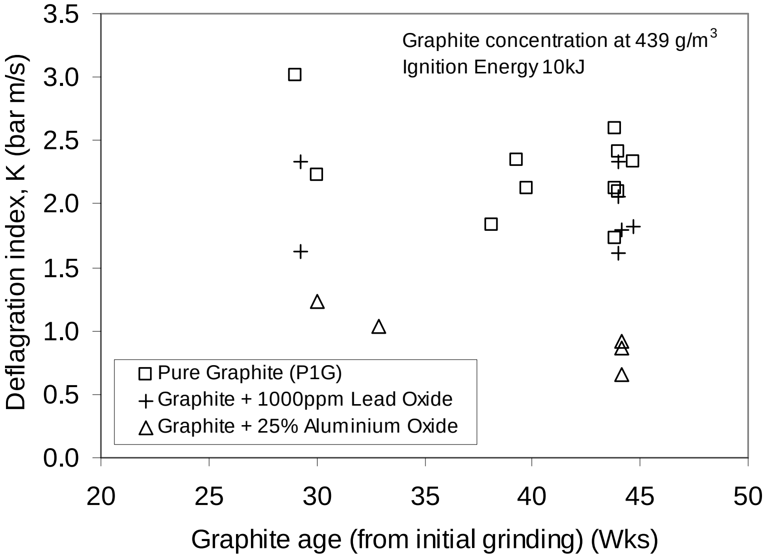


Figure 4-20
Illustrating the lack of effect of catalysts on deflagration index, in combination with the ageing effect

Lead oxide has potential catalytic effects, which may influence the ease of ignition of graphite. However, catalytic effects do not normally influence flame propagation in explosions as these are driven by kinetic reactions at high temperature in the flame front. Catalytic effects lower the temperature at which chemical reactions occur, but there is no low temperature basis on which explosion flames can propagate (apart from the cool flame regime in rich hydrocarbon explosions). As the pressure rise in an explosion is controlled by the temperature rise at the flame front and a catalyst cannot make this higher than thermodynamics will give, it may not be surprising that lead oxide has no influence on the explosion overpressure.

Five deflagrations were undertaken with graphite powder mixed with 25 wt % alumina powder (Al_2O_3). These results are also shown as a function of the graphite age from milling in Figs. 4-19 and 4-20. These results show that alumina mixed in at 25% by weight with the graphite gives significantly lower overpressures and reactivity K and the differences from graphite are well below the scatter of results for graphite alone for the same age. In Figs. 4-19 and 4-20 the overpressure and reactivity at 44 weeks is reduced from an average for graphite of about 0.25 bar overpressure and a K_{st} of 2 bar m/s to a 0.02 bar overpressure and a K_{st} of 0.8 bar m/s. The very low overpressure is most significant as this indicates a reduction in overpressure due to the addition of 25% of alumina by a factor of 10. The overpressure results indicate that the duration of the initial mass burn rate was comparatively short and hence the flame was extinguished at a relatively small size. Alumina at this concentration is clearly an *inerter*.

The mechanism of this overpressure reduction is due to the additional heat sink effect provided by the inert alumina. This is the same effect that explosion suppressant systems work on – for example, coal-dust explosions can be extinguished using injection of limestone dust ahead of flames. The mixing of limestone dust with coal dust is used experimentally to achieve a reduction in reactivity. For hydrocarbon flames the temperature has to be reduced below 1500K, by heat extraction, for the flame to be extinguished. Typically, for coal dust, 80% stone dust and

20% coal is ‘just reactive’. A key factor is that the effect is not catalytic and there has to be a significant mass of inert dust relative to the mass of reactive dust for the inerting to be effective.

4.5 France

The principal French studies into graphite dust deflagration are documented in reports from INERIS (Institut National de l’Environnement Industriel et des Risques) [49] and from CNPP (Centre National de Prévention et de Protection) [50, 51]. The initial INERIS studies were undertaken to support the proposed long-term storage of the graphite cores within the pressure vessels of the reactors: subsequently, the issue has been more comprehensively addressed with specific reference to decommissioning activities.

4.5.1 INERIS Studies

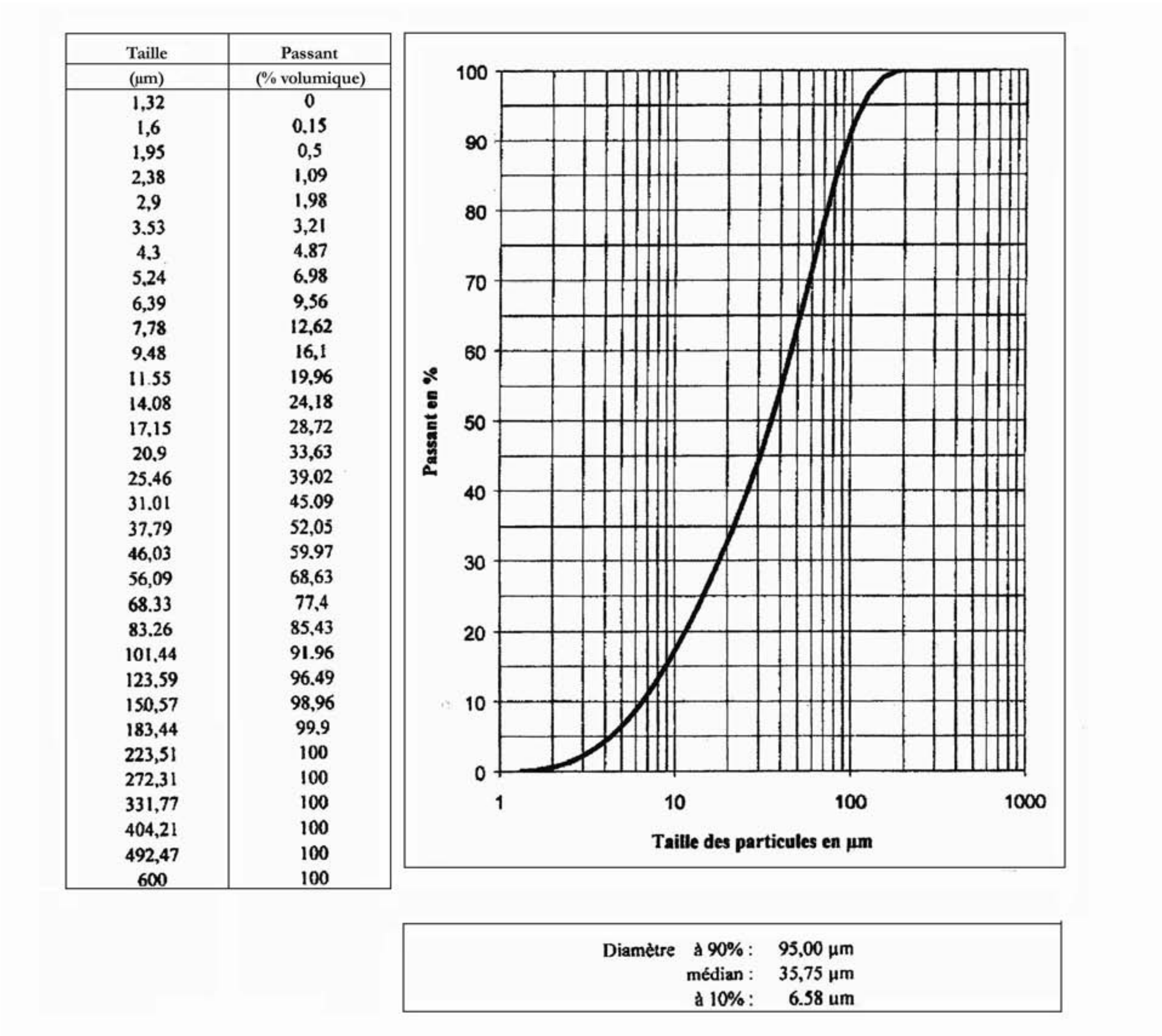
These studies commenced with an evaluation of the auto-ignition risk using thermogravimetry, determination of K_{st}, and evaluation of the particle size and water content of the pulverized sample. In the preamble, note is made of an un-referenced theory attributed to Frank-Kamenetskii which relates the ‘characteristic dimension’ of the powder (which might be an average particle size) to a function of the oxygen concentration and a ‘shape factor’, possibly the agglomerated form of the deposit on the surface, along with the activation energy for the oxidation reaction and some other property-dependent constants. The value of this citation in the present context, without further identification of the appropriate parameters, is doubtful.

In common with the studies already discussed, Ref [49] also includes in its introduction a comprehensive review of the conditions necessary for the establishment of a dust deflagration. One point of note is a comment that the lower explosible concentration limit for a dust is usually of order 50 $g.m^{-3}$, although this appears more of a general observation than a specific reference to graphite. Particular note is made of the ability of a hot surface to act as an ignition source, whilst it is also noted that a ‘minimum electrical energy for ignition’ can be defined for every (powdered) substance.

4.5.1.1 Granulometry

The graphite for the INERIS studies was provided in the form of a triangular bar by EdF. This was initially crushed to provide pieces of nominal dimension 50 mm, and these were then ground under nitrogen to give a sample of dust specified as < 0.1 mm.

The precise granulometry was determined using a Malvern Instruments laser machine type 2600C, according to the principles of a French national standard NF X 11-666. The particle-size distribution which was achieved is shown in Figure 4-21:



Taille (µm)	Passant (% volumique)
1,32	0
1,6	0.15
1,95	0,5
2,38	1,09
2,9	1.98
3.53	3,21
4.3	4.87
5,24	6.98
6,39	9,56
7,78	12,62
9.48	16,1
11.55	19.96
14.08	24,18
17,15	28,72
20.9	33,63
25.46	39.02
31.01	45.09
37,79	52,05
46,03	59.97
56,09	68,63
68.33	77,4
83.26	85.43
101,44	91.96
123.59	96.49
150,57	98,96
183,44	99.9
223,51	100
272,31	100
331,77	100
404,21	100
492,47	100
600	100

Diamètre à 90% : 95,00 µm
médian : 35,75 µm
à 10% : 6.58 um

Figure 4-21
Particle Size Distribution of Graphite from EdF Used in INERIS Studies

It may be seen that approximately 7% of the material is sub 5 µm, approximately twice that of the Italian sample but significantly less than that found in the material used in the later stages of the UK work at Leeds University. By monitoring the weight-change in the material held at a temperature of 104ºC, it was determined that the moisture content was lower than 0.1%.

Differential thermal analysis (risk of auto-ignition)

The determination was made in a standard suspension thermobalance between 25 and 800ºC, with a rate of temperature rise of 5K.min^{-1}. An inert substance was also present, in order to allow the generation of heat by exothermic reaction in the graphite sample to be determined by difference between temperature sensors in the two materials. Three runs were conducted in which the behavior of the graphite powder was compared with powdered carbon fibers and powdered coke:

Sample	Furnace Temperature at Onset of Weight Loss	Furnace Temperature at First Sign of Exothermic Reaction	Furnace Temperature at Which Differential Temperature Between Sample and Inert Reference Reached 50k	Maximum Rate of Temperature Rise in Sample	Weight Loss After 'Combustion'
Graphite powder	600ºC	540ºC	602ºC	90 K.min^{-1}	~ 0%
Powdered Carbon Fiber	595ºC	530ºC	595ºC	400 K.min^{-1}	~ 0%
Powdered coke	400ºC	280ºC	395ºC	90 K.min^{-1}	37%

The conclusions of [49] with respect to graphite powder are that it has approximately the same 'reactivity' as carbon fibre and very much less than coke, which is nonetheless categorized as 'low reactivity'. Since INERIS has much greater experience of coke behavior than nuclear graphite, it suggests in [49] that a relationship for the auto-ignition of coke-dust deposits based upon the Frank-Kamenetskii theory could be used "with a very large margin of security" if applied to graphite. This graph for coke powder is reproduced in Figure 4-22:

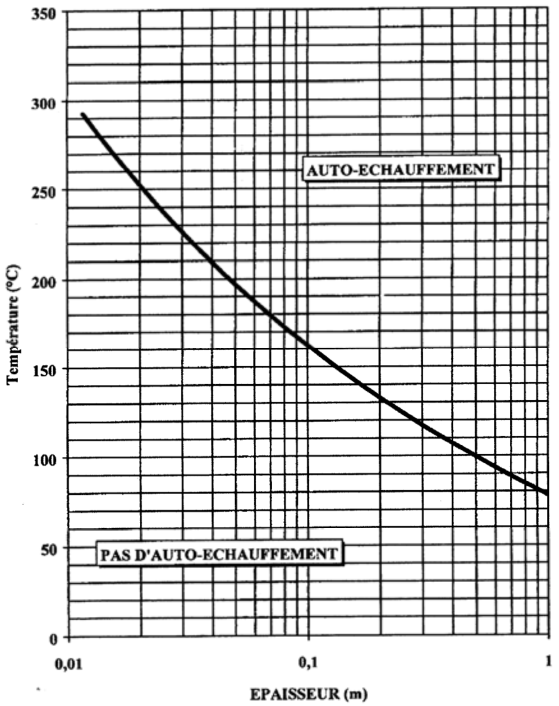


Figure 4-22
Graph showing the auto-ignition of a moderately-reactive coke powder as a function of thickness ('Epaisseur'): there is auto-ignition ('Auto-Echauffement') above the line. Ref [49] opines that this relationship could be applied to nuclear graphite powder "with a very large margin of security"

Explosion parameters

INERIS employed a standard 20-litre vessel for these determinations, using a pair of chemical igniters of total energy 10 kJ. The individual energy of one igniter, 5 kJ, is rather quaintly compared with the energy afforded by striking all of the matches in a box simultaneously. The experiments recorded maximum overpressure and (dP/dt)max for a range of concentrations of graphite dust: we calculate Kst[18] from the latter utilizing the vessel volume of 0.02 m3:

Dust concentration (g.m^{-3})	**60**	**125**	**250**	**500**	**750**	**1000**	**1250**	**1500**
Maximum overpressure (bar)	0	5.3	6.7	5.8	4.4	4.1	4.3	3.6
$(dP/dt)_{max}$ (bar.s^{-1})	0	35	250	235	170	60	265	50
K_{st} (bar.m.s^{-1}) (calculated by present authors)	0	9.5	67.8	63.8	46.1	16.3	71.9	13.6

Ref [49] identifies the minimum explosible concentration of graphite dust as lying somewhere between 60 and 125 g.m^{-3}, the maximum overpressure occurring at a graphite-dust concentration of 250 g.m^{-3}, and the maximum rate of rise, or K_{st}, corresponding to a dust concentration of 1250 g.m^{-3}. The result at 1250 g.m^{-3} concentration might, however, be considered anomalous, since the data break from a clear trend which sees all parameters otherwise peak at around 250 g.m^{-3} concentration.

The Italian work also covered concentrations up to 1250 g.m^{-3} and found no such second peak in $(dP/dt)_{max}$; indeed their work confirms that the peak in both reported parameters occurred at a concentration of around 250 g.m^{-3} as found here for the maximum overpressure and as inferred from the remaining data for $(dP/dt)_{max}$. We therefore consider that, on balance, the true maximum rate of pressure rise was found at 250 g.m^{-3} and that the result at 1250 g.m^{-3} is an experimental anomaly. However, it is worth also reconsidering the data from Leeds University (UK) in Figure 4-14. Here, too, maxima in both parameters were found at around 250 g.m^{-3} although there is a suggestion, albeit based upon one determination at 450 g.m^{-3}, the highest concentration used in the UK work, that a subsequent rise in parameters, especially K_{st} and hence in $(dP/dt)_{max}$ might have occurred.

Therefore, whilst the possibility cannot be entirely dismissed that the INERIS result at 1250 g.m^{-3} is genuine, it breaks a clear trend in data for which there is a precedent and there is no logical explanation for encountering one such high $(dP/dt)_{max}$ result in this fashion.

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[18] Whilst the French definition of K_{st} does not differ from the standard usage, it may be helpful to note that the definition appears in the official recommendation VDI 3673 (October 1983) but in the experimental standard AFNOR U 54-540 (December 1986) it is cited as K_{max}.

A comparison is also given of typical literature values of K_{st} and the maximum overpressure found for graphites from a variety of sources which, in general, support the view that typical figures are around 70 bar.m.s^{-1} and 5.5 – 6.5 bar respectively. These data only allowed the minimum ignition energy to be placed somewhere in the range 100 – 10,000 Joule.

On the basis of the results obtained at INERIS, this graphite dust is classified as weakly explosible (classification St_1) under the French standard VDI 3673, and gives about the same reaction as carbon-fiber powder which was studied in parallel to this work.

Additional information

Ref [49] includes a short bibliography of mainly French documents (although early work in support of the UK WAGR is mentioned) from which some useful information may be cited here. A CEA report [52] predicts a total of 16.7 tonnes of deposits (polymers of carbon suboxides of an uncharacterised nature) arising from radiolytic reactions in the coolant of the Saint Laurent A1 reactor. UK experience in Magnox reactors would suggest that the majority of this material is closely associated with graphite and would not be ‘loose’ within the reactor circuit. This quantity of deposits is approximately 0.63% of the weight of the graphite blocks, and ref [52] concurs with the UK view to the extent that the maximum mass of deposit on some graphite surfaces reaches 5.37%, presumably from monitoring tests. Thus, although this total quantity of reactive deposit may sound alarming in ‘dust’ form, and its chemical reactivity is likely to be higher than that of ‘pure’ graphite, it does not necessarily represent a significant explosibility risk.

EdF have separately assessed a settled powder content of 277 kg on and around the floors of the steam generators which occupy the lower half of the Bugey 1 reactor vessel, according to [49]. EdF additionally advise that this powder has a size range between micrometric and centimetric; some of it is carbonaceous, some metallic. The graphitic part is thought to arise mainly from splitting of biological protection blocks as a result of the corrosion of steel inserts. A rationalized extrapolation on all surfaces in the reactor of the observations made on the accessible bottom raised the figure to a few (about 4) tonnes of dust.

A second CEA note [53] reviews potential risks of pyrophoricity of graphite dusts and debris when removed from the storage ponds in which fuel-element graphite sleeves from the St. Laurent A reactors were deposited, and found no risk. Other technical notes mentioned in [49] cover issues of Wigner energy, and graphite purity, and are of only minor interest in the present context.

The summary of [49] does not elaborate on possible mechanisms for the generation of graphite dusts (*e.g.* from friction in fuel-handling chutes), commenting only upon the possible toppling of graphite blocks and noting (without reference) that it takes more than three times the energy to pulverize graphite than it does to pulverize granite to the same granulometry. On the other hand it makes extensive reference to the suspension of existing dusts and potential sources of ignition energy, and also correctly identifies the role of materials such as metal oxides in inerting the effect of a deflagration through absorption of heat.

Three residual uncertainties were identified in the view of the INERIS laboratory:

the influence of the particle-size distribution and the chemical composition of the dusts likely to be encountered on surfaces within the reactor vessel;

the minimum energy for ignition of a graphite dust cloud; *and*

the energy of mechanical sparks which might be generated during handling and dismantling operations, and their effect on any suspended graphite deposits.

In the context of [49], namely the 'safe-storage' of the reactor cores within their original pressure vessels for an extended period, attention was also drawn to the risks of secondary (dust) explosions should an explosive gaseous atmosphere be generated, and of the creation of potentially explosible dust clouds by falling objects.

4.5.2 Program in Association With CNPP

EdF-CIDEN made a commendable decision to explore the dust-deflagration issue further by seeking to replicate a real engineering situation with suspended graphite dust and a considerable ignition energy, with the objective of providing a convincing practical demonstration of the essentially benign nature of graphite dust. One of the present reviewers (AJW) was a consultant on the development of these final stages of this program, which was undertaken by the 'National Center for Protection and Prevention' (CNPP) in association with an EdF site at Moret-sur-Loing (" Les Renardières"), near Paris.

4.5.2.1 Phase 1

As a first step, CNPP conducted some additional basic studies [50] to confirm the initial INERIS results. The basic combustibility of graphite dusts was compared with that of graphite, utilizing a simple ceramic 'boat' and a muffle furnace. The samples were as follows:

solid graphite;

graphite dust in the range 100 – 400 μm;

graphite dust < 45 μm;

graphite dust < 15 μm;

graphite dust (70%) with iron dust (30%), all < 45 μm.

The last item was included to mimic the possibility of rupture of a powder-torch hose during cutting of components within the reactor.

In each case, the temperature of the furnace was raised from ambient to 900ºC at a rate of 3 – 4 $K.min^{-1}$ and the extent of mass loss noted. As these conditions, in an essentially free supply of air, would be expected to result in significant oxidation of bulk graphite, let alone dusts, it is perhaps unsurprising that these materials all suffered significant mass loss, with some 32% loss from the solid graphite, and total oxidation of the samples with particle sizes of 45 μm or less.

Just 54% mass loss however occurred in the case of the mixture with iron powder, but this could result from total loss of the carbon if the iron is oxidized to Fe_2O_3.

Overall, these test results are unsurprising. A significant oxidation rate was first observed with the dust at a temperature of around 580ºC.

CNPP also conducted tests with graphite dust preheated to 850ºC, following which they then utilized (i) an oxy-acetylene torch, and (ii) dropping molten metal. The first caused the dust to become suspended and ignite, which is essentially unsurprising, whilst the molten metal had no effect.

With dust at ambient temperature, a sample was then saturated in hydraulic oil following the French absorption standard NF T 90-361. It is to be noted that the reporting of this work in [50] is erroneous, and the correct ratios of oil to graphite are 173: 100 by weight for the graphite of 100 – 400 μm granulometry and 215:100 for that of 45 μm material. Thus, the dusts became aggregated with more than their own mass of oil under the specified conditions (essentially immersion for 20 minutes followed by draining for 30 minutes). The oil-soaked dusts of each of the specified granulometry were then each subjected to the flame of a "camping-gas" burner, and to particles of molten steel produced by a blowtorch, by arc welding, and by a grinder. Each of these processes, except for the grinder, produced some ignition of the oil-soaked material. With the camping-gas burner, applied for 30 seconds, it was slow: with the other methods producing molten metal, there was extinction in less than 10 seconds except for the intermediate particle size (< 45 μm) which took up to one minute. The reason for this is not understood. Propagation of the flame beyond its initial area was negligible.

The final test done in this preliminary CNPP work was to inject dusts into a vertical cylinder containing an open flame at the base, in order to compare the behavior of graphite dusts of various granulometries with that of iron dust and the standard maize flour. The dusts were blown from a 100g heap in small 'puffs' into a cylindrical aperture in the side of the bottom of the cylinder using an air gun. The initial flame height was approximately one third of the height of the cylinder, which was a 60 cm long sleeve with a triangular opening at the base.

There were three thermocouples at different heights within the cylinder. Only the lowest of these recorded changes of significance. From an initial temperature of 670ºC, graphite of all three granulometries, and the graphite/iron mixture produced a temperature increase to 750ºC, whilst iron powder alone produced 800ºC and maize flour 900ºC. Flames were emitted from the top of the cylinder only with the iron powder and, more significantly, with the flour: graphite/iron – approximately 30 cm in height above the top of the cylinder, iron alone approximately one metre, and with maize flour 1.2 m.

Whilst these initial CNPP tests do not constitute a suitable matrix of tests to provide an envelope for assessing the behavior of the graphite dusts comprehensively, they are in accord with the observations from other laboratories. Ref [50] concludes that graphite dusts of fine granulometry may be inflamed under certain conditions (*e.g.* oil soaking) and that suspended dust at a concentration of at least 60 $g.m^{-3}$ may be inflamed if a sufficient energy source is present. Nevertheless, the dusts are low in reactivity with air in comparison with iron powder and maize flour.

4.5.2.2 Phase 2

This second phase of the CNPP work, documented in detail in [51], was itself conducted in two stages. The first covered the development of an opacity methodology for the determination of dust concentration in air, and the second the utilization of high-speed photography to study the propagation of flame fronts in a ‘semi-confined environment’ - a transparent pipe of size comparable to realistic situations likely to be encountered in decommissioning a commercial reactor – essentially with the objective of proving that, even if a major ignition source were present and a suspension of fine graphite dusts occurred, a flame front moving along a pipe of typical plant dimensions would be self extinguishing. It is with this final study that one of us (AJW) was engaged[19], and it was developed with the recognition that routine studies in equipment such as the ISO vessel, although important, were not directly representative of the conditions to be encountered in reactor decommissioning.

The development of the opacimeter was also conducted in a plexiglass tube, vertically mounted and with a capacity of 200 litre.

Figure 4-23
CNPP apparatus for the determination of the relationship between opacimeters and graphite dust concentration

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[19] It is felt important to note here that this consultancy was limited to the general design of the tests and not with specific operational decisions such as the use of specific graphite concentrations or the removal of the opacimeters, discussed later.

The vertical tube was mounted on a closed plexiglass base and the upper end was closed by a further transparent plate. Graphite dust was introduced by a pulse of air delivered to a reservoir of graphite dust such that it was discharged around a circular tube at the base of the plexiglass tube. The injection system was extremely efficient and the average concentration of dust in the vessel could be calculated accurately. The tube was fitted with an upper and a lower opacimeter, each consisting of opposed light emitters and receivers linked to a simple electronic measurement system. The test allowed the determination of the relationship between the dust concentration and the light transmitted, which is the difference from 100% of the opacity value.

For the opaciter studies, UCAR graphite grade GS45E[20] was used to prepare a powder of which 90% was < 49.53 μm (30% lay between 25 and 45 μm, 31% between 10 and 25 μm and 29% < 10 μm). The density of the settled but unpacked powder was

0.34 g.cm^{-3}.

After ‘zeroing’ the output of the opacimeter, the valve was adjusted to blow in the dust, and the gas pressure was maintained for 10 seconds to ensure the best possible mixing of the dust with the air inside the tube. Numerous injections were made, exploring the best separation of the emitters and receivers, which was eventually set at 10 cm for the formal calibration tests. Some systematic differences were observed between the readings of the upper and lower opacimeters, the lower one consistently showing a greater reduction in light transmission that the upper one, indicative of a slightly higher dust concentration in the lower part of the tube, explained in [51] in terms of the mode of dust injection. The maximum recorded relative difference was 27% at a mean dust concentration of 25 g.m^{-3}. There was also a modest scatter in all data which was, however, not sufficient to obscure this systematic difference. A ‘global’ average of all measurements, including both detectors, was utilized in forming the relationship between concentration and opacity.

The formal calibration utilized dust concentrations of 25, 50, 100 and 150 g.m^{-3}. At this highest concentration it was clear that the instrumentation was approaching saturation, and this represents an upper concentration limit for this detector system unless it is possible to place emitter and receiver much closer together. The relationship in Figure 4-24 was obtained:

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[20] This grade of graphite is not utilised in any French reactor system, nor indeed, in any of the others facing decommissioning in the other nations participating in this comparison. However, this is not regarded as significant in terms of the performance of the dust.

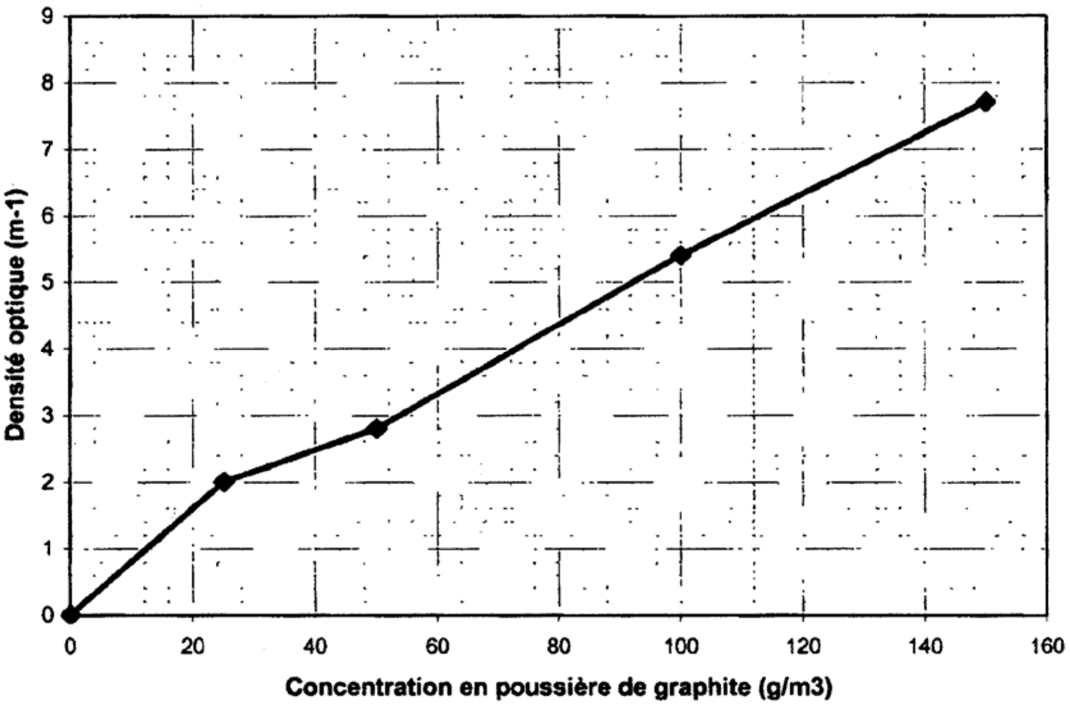

Figure 4-24
Opacimeters with 10-cm separation between emitter and receiver: relationship between graphite dust concentration and optical density

Two opacimeters were incorporated into the design of the large horizontal plexiglass tube used for the major part of the experimental program.

This tube was a little over 4 metres in length, approximately 50 cm diameter and with an internal volume of 742 litres. In this case, a two-section dust-injection system was employed to ensure an even distribution of material throughout the tube. In each half of the tube, a metal channel was placed containing evenly-distributed graphite dust. Across the top of each channel passed a perforated pipe, the air pulse emitted from it blowing downwards on to the channel of graphite dust, rapidly raising a quasi-uniform dust cloud. At one end of the tube was the ignition system, which is discussed below. At the opposite end of the horizontal tube, a pressure-relieving filter system was installed.

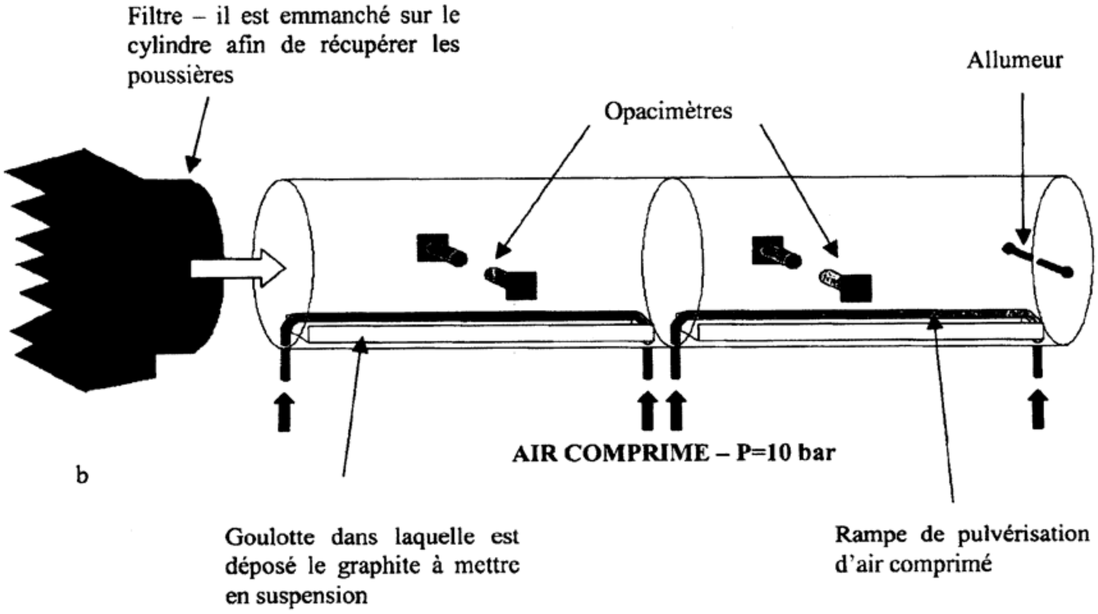

Figure 4-25
The CNPP flame-propagation apparatus, showing the position of the igniters ('Allumeur'), graphite-dust channels ('Goulottes'), air-injection system, pressure-relieving filter, and opacimeters

Figure 4-26
Detail of Gas-Injection System and Graphite-Dust Channel

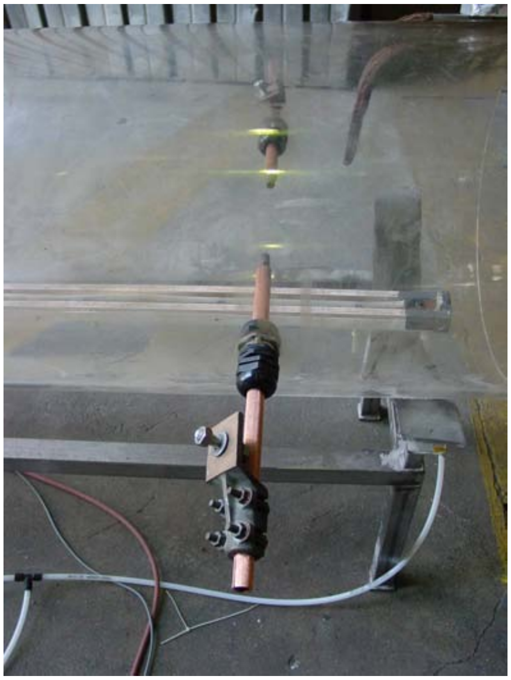

Figure 4-27
Detail of Electrodes Used for Ignition

Figure 4-28
General View of CNPP Apparatus in Position at Les Renardières

The electrodes consisted of graphite covered with copper at a spacing of 16 cm, disposed 35 cms from the closed end of the plexiglass tube. The arc was initiated between the electrodes with the aid of a fusible silver filament. The arc was driven from a 430V AC source at 14 kA, for durations of 10, 20 or 30 milliseconds, corresponding to an input of 60, 120 and 180 kJ. Clearly, these energies are much larger than those utilized in, for example, the standard ISO test, but were chosen such that the range encompasses three possible accident scenarios: (i) an electrical breakdown in a robotic handling device operating at 410V and 30 kW; (ii) the same in a remote platform at 75 kW; and (iii) a plasma torch operating at 720 kW and 230V.

Indicative measurements of temperature and pressure within the apparatus were effected in order to allow comparison of the nature of the pressure and temperature waves under different conditions.

The progress of each test was recorded using a high-speed camera system operating at 250 images per second: this has enabled some remarkable and convincing images of the relative performance of different dusts to be recorded.

A strict protocol was followed between tests. After each one, the apparatus was thoroughly cleaned and wiped out, with removal of all residual powder. The channels were then carefully re-filled with the appropriate amount of powder for the next test. For tests with graphite this was generally 480 g. A new silver filament was attached to the electrodes, and the length of the tube beyond the electrodes was shielded with a polyester plaque. The filter was replaced if necessary. The opacimeter trajectory was checked to be 10 cm and the zero of optical density re-set.

Next, the voltage, intensity (current) and duration of the required electrical arc were set, the time of air injection to suspend the powder and the interval before ignition were pre-set and the camera pre-trigger set, such that it would commence recording a few milliseconds before the ignition arc was struck. For the principle tests, 3.5 seconds were allowed for suspension before the arc was triggered, and the air injection was maintained for a further 3.5 seconds.

The apparatus was initially calibrated with a fine wheat flour, 'Francine Fluide', using a 330V arc, 5 kA current, a 10 ms arc, four seconds of suspension before striking the arc with the air injection maintained for a further three seconds. 1460 g flour was used (slightly under 2000 $g.m^{-3}$ if all was suspended). In accordance with expectations, the discharge caused ignition of the flour, with propagation along the length of the tube with a pressure pulse sufficient to damage the filter system slightly. A comprehensive video record of this exists to illustrate that the apparatus responds positively to a significant deflagration and propagation of the flame, in any strongly-explosible substance (see Figure 4-29)

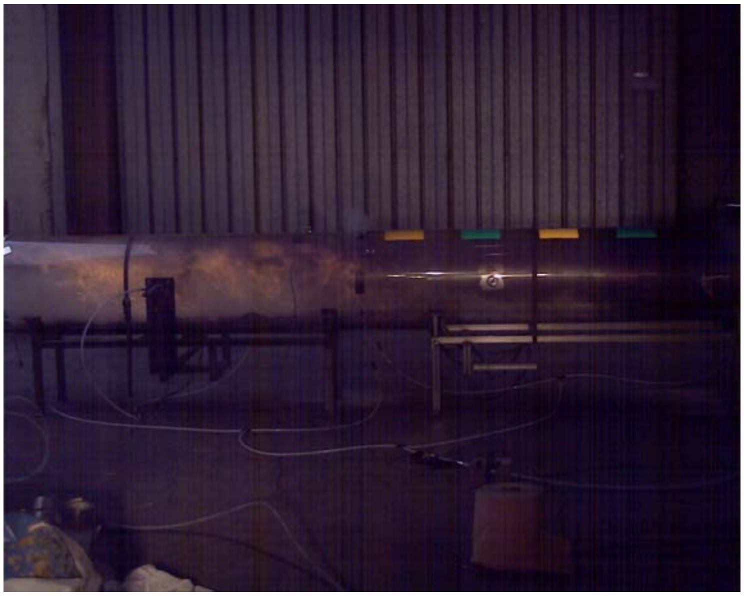

Figure 4-29
Propagation of flame front in wheat flour in the CNPP / Les Renardières Test, illustrating the expected performance of the test rig with a 'highly explosible' substance. Here the flame approaches the end of the tube having traveled a distance of approximately four metres

A point of significance regarding the behavior of the wheat flour was that the flame gained in intensity as it approached the 'open' end of the tube, indicating that it was receiving a better supply of oxygen at that time and, hence, that there was some oxygen deficiency within the tube during the ignition of the flour. A period of latency took place after the brightness of initial heat subsided: with graphite this ended with complete extinction, whereas in flour tests it was followed by a renewal of the combustion. This latency might be associated with a progressive deepening of oxidation within each particle, which was prevented in graphite by high thermal conductivity and lack of volatiles.

The principal results obtained using graphite powder are recorded in the following Table: in each case, a corresponding test utilizing the same ignition parameters was recorded with air alone. This was necessary for comparison purposes because the discharge at the electrodes was sufficient to vaporize some graphite, admixed with copper, to give a visible ball of flame in the vicinity of the electrodes. In the video records of which an example is given in *Appendix C,* each image is therefore a composite showing the system at the same elapsed time with and without graphite.

At this stage of the studies, the graphite source was crushed unirradiated fuel-sleeve graphite from batches intended for either the Chinon or St. Laurent reactors.

Test	Medium	Arc Energy (kJ)	Duration of Arc (ms)	Duration of Iincandescence (ms)	Maximum Distance Traveled by Flame (m)
914	Air only	59.5	9.9	80	0.90
915	Air only	62.5	9.8	76	0.83
3006	Graphite	65.2	10.0	156	1.04
3007	Graphite	70.2	10.2	104	1.16
909	Air only	113	19.3	156	1.28
911	Air only	106	19.3	144	1.61
3004	Graphite	110	19.2	156	1.40
3005	Graphite	112	19.3	168	1.17
907	Air only	170	29.4	200	1.35
908	Air only	165	29.4	216	1.66
3002	Graphite	ND	29.4	508	1.91
3003	Graphite	164	29.4	500	2.25

As may be seen, the results are grouped by ignition energy, and shown alongside the corresponding results for air alone. This is an important comparison because the electrodes alone produce significant incandescence due to evaporation and oxidation of the graphite and copper, which moves along the tube. Thus, the results for graphite need to be viewed in comparison with this ‘graphite-free’ equivalent, and three sets of time-lapse photographs are shown below.

A further point of interpretation of this table is the final column – maximum distance traveled by flame. Generally, the observed flame travels a little further in the presence of the graphite. Since the graphite is oxidizable, and significant energy is initially transferred to the suspended material close to the electrodes, this is not surprising. However, inspection of the visual record then shows clearly that the flame front is slowed, and eventually extinguished with termination of oxidation, in contrast to the behavior of the wheat flour illustrated earlier.

A final significant point is that the standard concentration of graphite used in the tests – equivalent to 647 g.m^{-3} if suspended with 100% efficiency, which is unlikely – greatly exceeds the measurable range of the opacimeters, from which no usable data were therefore recovered. Indeed, [51] records that the opacimeters were also an obstacle to combustion and retarded the propagation of the flame, so it was decided to remove them altogether once their unfailing saturation (guaranteeing a concentration of graphite dust in excess of 150 g.m^{-3} and the general homogeneity of the dust suspension had been confirmed. By definition, this ‘confirmation’ must have been conducted with a lesser amount of graphite dust. The specific graphite concentration chosen is not adequately explained in [51]. It lies on the shoulder of the ‘peak’ identified by the

INERIS study, but not at a sufficiently high level to cover the apparently anomalous high result at 1250 g.m^{-3} which we have already challenged. It is assumed that the chosen concentration provided the best visual records, and this is important: the great value of this test is the absolute confirmation in a 'real' situation that a large-scale graphite-dust deflagration is self-extinguishing whereas a 'strongly explosible' material like wheat flour clearly produced a 'positive' result sufficient to blow out the filter[21] and cause (according to anecdotal reports) 'a number of little fires' on the floor area surrounding the apparatus.

It was also noted that the pressure signal was extremely weak, with changes of only a few millibars. Anecdotal remarks indicate a maximum pressure increase of 6.4 mbar for a 115 kJ ignition, accompanied by a sound 'approximating to 55 Hz' – in other words, a low-pitched *'whoomph'* rather than a sharp report as from a detonation. Whilst this behavior would be expected for a deflagration, there is reason to believe that this sound was associated with the destruction of fragments of the electrodes since it occurred in the absence of graphite, this being corroborated by the photographic evidence of the behavior of graphite dusts within the tube and by its resonance being correlatable with the length of the tube. It was also noted anecdotally that there was no significant temperature change recorded at the surface of the tube in any of the tests.

Three sets of stills from the high-speed photography were obtained, each corresponding to one zone of ignition energy from the above Table. The first compares runs 914 and 3007, the second 911 and 3005 and the final set 907 and 3002. In each case, the evidence for the extinguishing of the flame front in the presence of graphite is unequivocal. The conclusions of [51] in regard to this interpretation of this work may be summarized as follows:

> the zone of incandescence produced from the *electrodes* is of the same size in the reference tests with air alone as in the presence of graphite for the same energy input;
>
> in the presence of a graphite dust suspension, the graphite particles are initially heated by the electric arc and may reach temperatures higher than 1000ºC: in opposition to this effect, the presence of the graphite may also suppress somewhat the visible emissions from the electrical arc;
>
> the incandescence within the graphite dust then expands in volume as a result of the heating (some surface oxidation of the hottest particles also occurs, making a further exothermic contribution, and this contributes to an extension of the duration of the visible incandescence);
>
> the incandescence within the graphite dust suspension does not produce energy sufficient to compensate for losses through conduction, convection and radiation: in consequence the dust suspension cools and the incandescence is extinguished – this despite modest blowing of fresh air from beneath; *and*
>
> under the conditions of this experiment, there was no deflagration in the graphite dust.

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[21] In a number of cases the filter was also blown out in the tests with graphite, presumably through the pressure wave produced from the electrical arc.

Whilst this experiment, designed to allow reproducible testing conditions, was far from a 'perfect' replication of a realistic situation in decommissioning, the inability of such significant energy inputs to create a deflagration gives a large degree of support to the view of the present authors that there is no significant risk of encountering dust-deflagration issues in the course of decommissioning a graphite-moderated reactor.

4.6 Evidence From Other Sources

There is very little general literature relating to evidence or risk of graphite dust explosions, save for the basic texts such as Field [3] which has already been discussed in detail. In the course of this review, four major international graphite manufacturers operating in Europe, the USA and Japan[22] were asked informally whether there had ever been a dust deflagration associated with their processes, given that graphite manufacture involves baking at around 1300ºC and subsequent graphitization at around 2600ºC or higher, using gas ovens in the first stage and high-density electrical currents in the graphitization phase, with a dusty environment created from packing coke. None of the companies indicated that they had ever experienced any problem.

However, one major manufacturer, which we may not identify[23], engaged in a test program, principally involving the ISO apparatus, in 1996, utilizing a graphite powder of unspecified grade and of particle size simply stated to be <75 μm. An extensive series of tests was carried out, with concentrations in the range 60 - 1000 $g.m^{-3}$.

Using the specified 10 kJ igniters, the maximum explosion pressure found was

6.3 bar, with a graphite dust concentration of 125 g.m-3, the maximum rate of pressure rise found was 310 bar.s-1 at 750 g.m-3 (although these results were erratic with high results also occurring at 250 and 500 g.m-3 in separate test runs), and the maximum value of Kst was 76 bar.m-1.s-1, thus once again placing pure graphite dust of this granulometry in the category of a 'weak explosive'. The dust employed was found to have an extremely low moisture content.

The same material was then subjected to tests in the Hartmann-type capacitative-spark apparatus, nominally to the British Standard 5958 [54], in order to identify the minimum ignition energy. Again, in line with results found elsewhere, in a total of 140 tests using quantities of graphite powder up to 4 g, no ignition occurred. Strangely, the maximum spark energies are not recorded, it merely being recorded that an arc from a 10 kV transformer was used and that there were problems because the graphite powder short-circuited the arc. However, the energy must have been < 10J since the recorded result is that the ignition energy must lie above this value.

Tests were also conducted for minimum ignition temperature using a variation of the apparatus previously described, known as the Godbert-Greenwald furnace (see [24]). With furnace temperatures up to 800ºC and quantities of graphite up to 0.25 g there was no ignition.

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[22] SGL Carbon Ltd, GrafTech International, Inc., The Toyo Tanso Co. and Morgan Carbon Ltd.

[23] The nature of this arrangement is that we may utilise the data provided that the source is not identified, this being for reasons of commercial security.

Thus the results obtained for this company for graphitized material are fully in accord with the range of data assessed earlier in this review.

The only other significant relevant reference to address concerns about graphite-dust explosibility which we have located comes from an assessment by Framatome of the safety hazards associated with the pilot graphite-incineration plant constructed and operated at Le Creusot, France [55]. The report of the safety analysis within this reference is extremely brief, but it concluded that it was 'impossible' to obtain conditions under which there was a dust-explosion risk. The features considered include:

the lack of volatile material in the graphite;

the lack of any production of a significant proportion of fine particles ($< 75\ \mu$m) in the crushing process intended for graphite blocks introduced into the plant;

the maintenance of continuous ventilation in the crushing room to remove any such particles which might occur[24]; *and*

a risk assessment investigating 'precursor' and 'intermediate' events that could lead to operating incidents, resulting in the incorporation of appropriate detection and alarm systems and operating procedures.

Thus, this represents an application of the principal of removing at least one of the parameters needed to be simultaneously present to allow a dust explosion (albeit in a superficial analysis) together with an understanding of some specific properties of the graphite which also mitigate against the risk. It is far from a comprehensive treatment, insofar as the publication is concerned, but the principles and findings accord with the general consensus achieved by the other work reported.

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[24] This point is amplified in a confidential Framatome report produced to support a proposed incineration project for St. Laurent reactor fuel sleeves *(private communication)*. This identifies the major risks in pulverising the graphite for incineration as the combustible gas used for pre heating (propane) and production of poisonous CO from the plant, suggesting that the crushing room should be contained equivalent to Class 2 leak tightness (< 0.01 vol.h^{-1}), with suction at points where dusts might be generated.

5
DISCUSSION AND REVIEW

5.1 Basic Studies

Each organization participating in this review has included in their earliest researches some simple tests involving layers of graphite dust subjected to impinging flames, falling debris from cutting operations, etc., and in most cases also with hydraulic or other oils soaking the graphite. In each case, it was found that settled dusts did not represent a hazard from cutting torches unless oil was also present, when it was found that the oil would vaporize, sometimes with ignition and visible flames, but that this would not result in ignition of the dust. Incandescent particles from cutting and grinding were never able to ignite the oil, although those from arc welding did so in the CNPP studies.

The poor ignition quality of incandescent swarf from grinding operations etc. is discussed in *Appendix A*, and this is entirely consistent with remarks in a reference about general dust ignition, not specific to graphite, commenting that the minimum size and temperature at which an incandescent particle *could* represent a hazard to settled dusts (of general explosible character) is about 3 mm or larger, with a temperature in the range 600 - 800ºC [56]. At smaller sizes, radiative heat losses from the swarf particles, coupled with conductive losses upon contact with the colder dusts, ensure that they represent no hazard.

It therefore appears that the greatest theoretical hazard associated with settled graphite dust during decommissioning is that it becomes suspended either through objects falling on to it or displacing it, or as a result of some separate primary explosion event which causes a turbulent pulse in the atmosphere above it. It is interesting that the gases from cutting torches did not easily suspend settled dust in every case, even when impinging directly upon it, probably as the result of the tendency of particles to be attracted to one another, especially if the atmosphere is slightly damp. Suspension (and ignition) occurred in the French and Italian work with an oxy-acetylene burner. However, as other parts of the programmes have clearly demonstrated, suspended graphite dust clouds themselves present an extremely low risk.

5.2 Fundamental Explosion Parameters

5.2.1 Granulometry

In making comparisons between the behaviors of graphite dusts in different studies, it is first necessary to comment upon the granulometry of the different samples. This is considered to have a much larger potential effect upon behavior in any deflagration than the original nature of the graphite from which it is derived, since the differences between graphite grades arise from the particle size in the original cokes, forming methods, extent of porosity etc – in other words, through effects on a macro scale which is greater by orders of magnitude than the size of the more reactive dust particles, which are considered to be those < 5 μm on the basis of the British studies. However, it is useful to note that a range of different graphites have been included in the studies, including Pile Grade ‘A’ (a UK needle-coke extruded material), Lima (a similar grade used in French UNGG reactors), a UCAR grade used in fuel sleeves, and Pechiney grades of a slightly finer-grain material employed in the Japanese reactor at Tokai 1.

In comparing the granulometries, an estimate is made of the particle size at the peak of the distribution, and of the proportion of the dust lying below 5 μm:

Italy unirradiated graphite dust	peak > 100 μm; 1.5% < 5 μm
Italy reactor dust	peak ~ 20 μm; 4% < 5 μm
Japan ‘coarse’ dust	*defined as < 300 μm*
Japan ‘fine’ dust	*defined as <25 μm*
UK	peak 6 – 7 μm; 33% < 5 μm
France (INERIS)	peak ~ 60 μm; 7% < 5 μm
France (CNPP)	peak 23 –30 μm; ~10% < 5 μm

Clearly the UK dust, and possibly the Japanese ‘fine’ dust, are much finer than the samples used in the other studies, with the Italian material the most coarse. Whilst this has meant that the British workers have been able to reach conclusions about participating particle sizes which were not found in other work, it does not mean that the other work is in some way ‘inferior’ – indeed, it could equally be regarded as ‘more representative’ in the sense that agglomeration of small particles upon keeping the samples has also been noted, suggesting that the finest dusts, at least where utilized for testing quickly, could in fact be the unrepresentative samples.

In the opinion of the present reviewers, all the results presented are regarded as of equal merit, the differences in particle size distribution (whose influence was not necessarily foreseen) having served to highlight its importance. What should be borne in mind is that any differences in fundamental ‘explosion parameters’ in the different studies may be related to the particle size distribution and the age/history of the sample.

5.2.2 Minimum Ignition Energy

The Italian and Japanese studies are fairly unequivocal in agreeing that the minimum ignition energy under standard conditions for initiating a dust explosion in their graphite samples was around 2 kJ. The Japanese work confirms that the coarser sample was more difficult to involve in a deflagration. Early UK studies were only able to place the threshold somewhere in the range 100J – 20 kJ, but the more recent studies from The University of Leeds suggested a threshold in their ISO apparatus in the region of 4 –5 kJ. INERIS utilized a standard 10 kJ and obtained ignition.

Given the greater proportion of fine particles in the Leeds dust, it is perhaps surprising that they found a higher threshold ignition energy than either Italy or Japan. We consider that such a difference may be a consequence of fundamental differences in technique – the delay between dust injection and ignition, the efficacy of the suspension itself, vessel size – etc. It certainly suggests that finer particles, while oxidizing more thoroughly, are not significantly more prone to ignition. It is certainly reasonable to conclude that ignition of pure graphite dusts at an energy less than 2 kJ under the conditions of ISO, ASTM or equivalent standards, is extremely unlikely, and we therefore recommend that in the decommissioning situation, where possible, any potential ignition sources approaching this level of energy should be eliminated. With cutting torches present, this may well not be possible, and so we note that avoidance of the ignition source is only one of the potential courses of action open to the designers of a decommissioning scheme to mitigate against a potential explosion risk.

Whilst there is some effect of dust concentration on the minimum ignition energy, it is not generally sufficient to affect the conclusions reached. However, the Japanese data led them to conclude that there was no ignition at *any* energy if the dust concentration exceeded 250 $g.m^{-3}$: this is flatly contradicted by data from the other studies (and, indeed, from some of their own) and is considered to be an incorrect deduction arising from an insufficient matrix of test conditions employed in that study, the attention of the investigators apparently being deflected into variable oxygen concentrations before the basic understanding of the behavior with an atmospheric oxygen concentration was completed.

5.2.3 Explosible Concentration Range

As just stated, we feel unable to accept the Japanese conclusion that no concentration above 250 $g.m^{-3}$ is 'explosible' as this is contradicted by their own information and all of the other available data. Other work supports a threshold *minimum* 'explosible' concentration in the range 60 – 125 $g.m^{-3}$. Definition of the *maximum* value is more difficult from the data available: the Italian work suggested that at a concentration > 750 $g.m^{-3}$ a significantly higher ignition energy was required, but a positive result (weak deflagration) was still obtained at 1250 $g.m^{-3}$; early UK work gave a positive result at 500 $g.m^{-3}$ and the more recent studies included a single result at 800 $g.m^{-3}$; French data found weak deflagrations at the highest concentration used which was 1500 $g.m^{-2}$. Clearly, the explosible range of pure graphite dusts is potentially quite wide, although all deflagrations are weak and at the higher concentrations they are extremely weak.

5.2.4 Maximum Rate of Pressure Rise and K_{st}

For maximum rate of pressure rise, the Italian and UK studies are in close agreement, with INERIS from France returning a higher value. There are no appropriate data from Japan.

The derived value from the Italian reference [27] is 118 $bar.s^{-1}$, as previously discussed, but the highest value found was 167 $bar.s^{-1}$. Early work in the UK identified the value to lie in the range 147-157 $bar.s^{-1}$ whilst the later work at The University of Leeds gave approximately 130 $bar.s^{-1}$, all of these values being obtained with a 20 kJ igniter and at dust concentration at or below about 250 $g.m^{-3}$. INERIS (France) however found the maximum to lie at 250 $bar.s^{-1}$ if, as already proposed, we are permitted to ignore an apparently anomalous value of 265 $bar.s^{-1}$ reported at the very high dust concentration of 1250 $g.m^{-3}$.

However, the more useful comparison is K_{st} since this eliminates the complicating factor of differences in vessel size. The declared Italian result was 32 $bar.m.s^{-1}$ although the highest value measured in the sequence of tests was 45.3 $bar.m.s^{-1}$. The earlier UK work found results in the range 39 – 43 $bar.m.s^{-1}$, but the later work at Leeds raises a puzzling discrepancy. The ‘pure graphite’ results, considered rather inaccurate, gave just 14 $bar.m.s^{-1}$ whereas the result de-convoluted from the methane-driven tests for graphite alone is 61 $bar.m.s^{-1}$. With the benefit of hindsight, it is clear that the Leeds team were persuaded to favor the methane-driving technique because very weak deflagrations resulted from their graphite sample alone – however, the derived results from the methane-driven tests are unexpectedly higher than those obtained directly from the samples used elsewhere. The present authors derived 67.8 $bar.m.s^{-1}$ from INERIS tests.

What is perhaps most important here is not the absolute value, which will in any case vary significantly with concentration, granulometry, nature and age of the powder and precise experimental technique, but rather that all of these results are low and in the region which characterizes only a weak deflagration in the standard test regime (*i.e.* with 2 kJ chemical igniters present).

We also note that, although some tests report pressure reached during the combustion of graphite dusts of order 6 bar, these occur only in the small test vessels. Although Bartknecht [7] points out that the maximum pressure in a test vessel environment is largely independent of vessel size for a given dust concentration, in this less confined environment of a decommissioning situation, any pressure rise resulting from the combustion of graphitic dusts would almost certainly be in the mbar range.

5.2.5 Auto-ignition

The best information on this parameter comes from the Italian work at SSC, which found no susceptibility of their material to auto-ignition under the accepted definition used in that laboratory, with the sample temperature lagging behind (below) the furnace temperature when the latter was increased steadily over a period of 48 hours. The Japanese also found their sample to be self-extinguishing in a related test.

INERIS in France conducted a comparative study with other carbonaceous materials, but presented the data in a somewhat confusing manner, indicating only the temperature at which their sample exceeded the furnace temperature by 50 K, indicative of exothermic oxidation exceeding an arbitrary limit (602ºC) and indicating a maximum rate of temperature rise in the sample (to be compared with that of the oven). The data are interesting but require a more appropriate interpretation to be useful here. This was a very much faster test than the Italian work, with a temperature increase in the furnace of 5 $K.min^{-1}$. In the opinion of the present reviewers, such results are likely from any material which undergoes an exothermic reaction in a plentiful supply of air and is placed in a furnace whose temperature is ramped upwards this rapidly or to such a high value : auto-ignition is meant for ambient temperatures, hence the 140°C limit retained in the Italian work, whereas 600°C or so cannot be reached without a flame or another high energy source around.

The overall conclusion is that pure graphite dust does not exhibit any significant tendency towards auto-ignition.

5.2.6 Overall Summary of ‘Explosion’ Characteristics of Graphite Dusts

Whilst there are a small number of inconsistencies in observations, and a greater uncertainly in comparing specific numerical data because of differences in experimental conditions, granolometries etc., overall it is clear that all pieces of work using standard measurements of explosion parameters lead to the clear conclusion that pure unirradiated nuclear-grade graphite is ‘explosible’ with difficulty and undergoes an extremely weak deflagration.

5.3 Impure Graphite Dusts

With a single exception, all tests conducted using impure material, whether it be reactor-circuit dust (Italy) or with deliberately added material thought either to be an oxidation catalyst for graphite or a potential deflagrator in its own right (Japan and UK) have found the resulting dust mixture to be less reactive than the pure one. This is consistent with the added material acting as a heat sink and removing energy from the potential flame front. Certainly in the case of circuit dust, the impurities are likely to be in the form of fully oxidized metals. A related result, from Japan, indicated that it was necessary to use a larger dust concentration to obtain ignition in the presence of 5% FeO.

The ‘inerting’ effect of many impurities on the explosibility of combustible dusts has been known for many years, with the identification of the inert content of dusts in coal mines being an important part of the assessment of the overall explosion hazard [57]. The mining regulations generally require a *minimum* defined impurity concentration to be *exceeded* in order to ‘dampen down’ the explosibility hazard afforded by the coal dust, adventitious methane gas, etc. etc. In this case, the impurities are generally silicate minerals which have no propensity towards further oxidation.

The exception to this inerting effect as observed in the studies reviewed here is the effect of iron powder, selected by both the Japanese and the French investigators because of its potential presence in powder-cutting torches (which rely on the energy of its oxidation to raise the temperature of the cutting site). Whilst the Japanese tests with 5% iron powder did not appear to make ignition easier (or to lower the minimum dust concentration required for reaction), the CNPP tests in which iron powder admixed with graphite was introduced into a vertical inflammator caused a significant increase in flame height. It was clearly demonstrated that the iron powder alone would inflame much more strongly than the graphite powder.

Given the exothermicity of the oxidation of iron, and the well-known pyrophoricity of fresh finely-divided iron powder, this is in fact an unsurprising result. It indicates a need in decommissioning to guard against the eventuality of a powder-hose failure when using cutting equipment, but it would appear that the greater risk is from the escaping iron powder rather than from any secondary effect involving graphite, although we shall consider this issue again below.

5.4 Ageing

The only work to investigate systematically the effect of the ageing in samples of graphite dusts was The University of Leeds in the UK. Their work presents clear evidence that samples rapidly reduce in susceptibility towards undergoing dust 'explosions' with time, whether or not they are isolated from the atmosphere. The explanation offered is that agglomeration of the smaller particles takes place quite rapidly, and it is only the very smallest particles (< ~5 μm) which readily participate in the propagation of a flame front. The evidence for this is not unequivocal, and is partially based on inference. However, the results are reproducible, and strongly suggest that, in a decommissioning scenario, any graphite dusts present will have had ample time for the smaller, more reactive particles to be effectively lost.

This therefore represents an additional valuable piece of the argument to be made in decommissioning safety cases in relation to the dismantling of graphite-moderated reactors. Long periods of standing in air are also likely to increase the moisture content of the dusts, which also reduces their reactivity.

Additional work to quantify the ageing effect was suggested by The University of Leeds, along with other proposals for further studies with graphite in the dust-explosion area, but it seems unlikely that additional work in this topic area is justified.

5.5 Flammable and Oxidizing Gases

A limited amount of work has been conducted using enhanced oxygen concentrations, presumably on the basis that the oxygen supply in an oxy-acetylene burner or propane burner could rupture within a confined space during decommissioning activities. It is not surprising that the deflagration risk increases under these circumstances. The Japanese work extended to enhanced oxygen concentrations which are not entirely clear, whilst early UK work examined mixtures containing up to 90% oxygen.

There are insufficient data to correlate this information in any precise way, but it is clear that enhanced oxygen concentrations in the oxidizing gas associated with graphite dust are likely to assist the deflagration reaction significantly and should therefore be avoided. Appropriate safety considerations can be written into operation procedures for cutting using such equipment, and the use of automatic isolating valves in the oxygen supply which are pressure sensitive should be sufficient to interrupt the oxygen supply in the event of a hose rupture, thereby preventing the build up of additional oxygen in the reactor environment.

Conversely, one may elect to use an inert atmosphere in the vicinity of a cutting operation in any special situation.

The risk of introducing a flammable gas such as propane into the cutting environment is obvious, and can be mitigated in a similar fashion. The enhancing effect of a hydrocarbon gas in the air was demonstrated by the deliberate use of a methane driver in the recent UK work at Leeds University.

5.6 Wigner Energy

This represents a special situation which has not been examined directly in the work reviewed, but which is important in reactors (such as the UK Windscale Piles, the US Hanford reactors and the Brookhaven Graphite Research Reactor, etc.) which have been operated at low temperature. Such conditions allow a significant build-up of internal energy within the graphite crystallites as a result of interactions between the carbon atoms and fast neutrons, resulting in displaced atoms and vacancies in a variety of higher-energy structures compared with the original crystal lattice. In graphite irradiated throughout at higher temperature, concurrent annealing occurs by both thermal and irradiation-produced mechanisms, much of the potential energy content is lost and there is a tendency to saturation at a low total stored energy which is relatively inconsequential.

Where significant Wigner-energy build-up occurs, the greatest risk is that the potential rate of release upon heating exceeds the specific heat capacity of the graphite. If this happens, a spontaneous large rise in temperature occurs, and early reactors were subjected to periodic controlled annealing exercises in order to mitigate against this possibility. Unfortunately, the exact nature of the process was not fully understood in the early days, and the Windscale Pile No. 1 fire in the UK was a direct result of a mishandled anneal.

Fortunately, a spontaneous energy release is only possible if the conditions are close to adiabatic, and no measurable release is generally observed unless the graphite is heated approximately 50K above its irradiation temperature.

In the context of dust deflagrations, the significant issue for dusts formed from material which might contain Wigner energy is that they contain an internal energy source which can contribute heat once some initial heating from an external source has been established, sufficient to raise the particles at least 50K above their irradiation temperature. In a flame front, the initial rate of temperature rise is very high, and so the internal energy will simply be liberated with no significant delay.

The effective result of this is that the flame front will propagate more easily than in equivalent dust with no Wigner-energy content, since it requires less external energy input to achieve the same rate of flame propagation. Effectively, this makes the graphite dust appear to be more reactive in the oxidizing atmosphere, and thus such dusts will be relatively more ‘explosible’ than dusts with no Wigner-energy content.

In any situation where this might be an issue, a comparison can be made of the energy releasable from Wigner energy with that generated from the exothermic oxidation reaction. The former can be evaluated by routine techniques on bulk or powder samples, such as bomb calorimetry; the latter is known (see, for example, *Appendix A*). This will then give a measure of the potential increase in effective reactivity of the dusts should they be in a position to engage in a deflagration, and this information may be used to determine whether any special conditions need to be applied. As an example, the greatest Wigner energy content found in graphite from the UK Windscale Pile No. 2 (where no fire occurred, and perhaps approaching a ‘worst-case’ internationally) is of order 1 kJ.g^{-1}. This may be compared with a calorific value for unirradiated graphite of 32.6 kJ.g^{-1}. Thus, the effect of the Wigner energy would be measurable but remains a relatively minor contribution to the total energy release and thus the effect on flame propagation would be small. All other issues and conditions relating to the establishment and propagation of a flame front in suspended graphite dusts – presence of an ignition source, particle-size distribution, concentration etc. – continue to apply as usual.

5.7 Practical Decommissioning Situations

The large body of experimental data reviewed here leads to the clear conclusion that it would be extremely unlikely to be possible to achieve a dust explosion with nuclear-grade graphite dusts within a reactor undergoing decommissioning and, even if it were possible, it is rather easy to ensure than one or more of the critical conditions necessary to achieve such an explosion are not achieved. However, it is worth looking at some specific scenarios which *are* possible, and how they might be addressed in safety cases.

We envisage a decommissioning program which includes cutting of metal components adjacent to graphite and/or deposited graphite dust using cutting wheels or grinders, possible welding and flame cutting using gas torches, and the use of gas torches which include materials such as iron powder. We imagine that there is partial containment in place, but with opportunities for venting to atmosphere such that, in the event of an explosion, there is a possibility of short-term pressure increases, release of radioactive or particulate material into the atmosphere in an uncontrolled (un-filtered) manner, and movement of previously unsuspended material elsewhere in the circuit as a result of pressure pulses.

The tests conducted in the 50-cm diameter pipe at CNPP illustrate clearly that it is difficult to initiate a propagating flame front in such a geometry and that even with a large ignition energy sufficient to create such a front, it is self extinguishing on a very rapid timescale. This evidence is extremely valuable in giving reassurance that in practical situations, a deflagration involving graphite dust is extremely improbable.

Experience with the detailed safety analyses made, for example, in support of such decommissioning and dismantling of the graphite stack in the UK WAGR [58][25], suggests that the greatest safety risk is a propane-gas explosion within the vessel arising from either a hose rupture or the inadvertent extinguishing of a flame causing release of unburned propane/oxygen mixture into the vessel followed by re-ignition from an independent source after a body of unburnt gas has built up. Such a propane ignition would provide an ignition source for dusts, supplies ample heat, *and* suspends any dust present. It is therefore essential to engineer suitable pressure-sensitive cut-off valves into the gas supply lines to ensure that the propane supply is cut off in such an eventuality. A fuel-fed gaseous explosion giving rise to a secondary explosion involving dusts as a result of the pressure pulse and the movement of hot or inflamed gases is the most serious risk involving graphite dust. Whilst the University of Leeds work showed that secondary explosions involving graphite dust alone were extremely hard to achieve and could not be achieved at all in their simulation of the connected enclosures representing the Windscale

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[25] The published ref [58] is rather superficial, but UKAEA has made available to the present authors the full technical reports in which the safety case was argued, and our comments are based upon this more comprehensive treatment.

Pile, the presence of a significant hydrocarbon content in the vessel atmosphere would present a risk which should be considered when planning the operation and conducting a risk assessment.

A related risk is the rupture of hoses containing powdered iron, which is a strongly explosible dust. In admixture with any graphite dust, the risk of explosion increased, but in reality the iron powder itself presents a much greater potential risk, and it is towards avoiding any release of that material that attention should first be directed when planning powder-torch cutting operations.

6

CONCLUSIONS

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1. Extensive test programs have been conducted by France, The United Kingdom, Italy and Japan into the behavior of nuclear-grade graphite dusts in the presence of an ignition source. These programs have had common features which offer the chance to obtain independent confirmation of basic 'dust-explosion' parameters on a variety of samples drawn from graphites used in reactors now approaching decommissioning and, separately, two of the programs have included innovative experiments intended at investigating specific practical situations relevant to the decommissioning of graphite-moderated nuclear plant.
2. The results obtained for basic parameters have shown a high degree of conformity, confirming that pure graphite dusts are very weakly explosible under the conditions of an ISO standard or equivalent standard test. These standards require ignition of the material after suspension into a confined and known volume, utilizing chemical igniters of energy typically 10 – 20 kJ. Previously, such dusts had been reported as 'non-explosible' on the basis of older forms of apparatus employing much weaker ignition sources such as electrical sparks typically in the range 10 – 100J, and there is therefore no inconsistency in this altered definition. Standard methodologies such as the ISO test allow extremely useful comparisons between dusts of different composition but, in order to understand dust behavior in a practical engineering situation, more sophisticated investigations are appropriate.
3. Basic 'explosion parameters' for nuclear-grade graphite dusts of the particle-size distributions employed in these studies (intended to represent typical distributions of material within the reactor vessels) are as follows:

   Minimum ignition energy: ~ 2 kJ over a range of practical concentrations
   Minimum explosible concentration: in range 60 – 125 g.m^{-3}
   Maximum explosible concentration; poorly defined but >1500 g.m^{-3}
   Maximum rate of pressure rise in standard test: range 118 – 250 bar.s^{-1}
   Deflagration index: in range 14 – 61 bar.m.s^{-1} (with the most probable value lying around 45 bar.m.s^{-1}). A value of deflagration index anywhere in this range classifies the material as very weakly explosible.
4. Additives and impurities generally reduce the potential 'explosibility' of the graphite dust, especially when the impurity is fully oxidized such as metal-oxide residues from other parts of a reactor circuit. Potential catalysts of thermal graphite oxidation, such as lead compounds, have no specific effect because the oxidation of the dust appears to be governed by the available supply of oxygen at the flame front rather than by the chemical kinetics of oxidation at surfaces. An exception to this general observation was iron powder as used in powder-cutting torches: this is extremely reactive as a dust and care needs to be taken to avoid any release into the reactor vessel if such technologies are used in decommissioning.

5. When a deflagration does occur with graphite dust, a significant amount of the dust remains unburned. Research in the UK has shown that only particles with diameters less than around 5 μm participate in the dust deflagration, larger particles behaving as heat sinks and reducing the potential of the flame front to propagate. The same work also demonstrated that, except in freshly ground samples, smaller particles tend to agglomerate such that in periods of 30 – 40 days, the potential reactivity of any sample is greatly reduced. Thus, the presence of fine particles would not be expected in dusts collected within reactors. Moisture also acts to reduce reactivity and to encourage agglomeration.
6. The behavior of graphite dust in practical engineering situations has been investigated in both the UK and France. These tests demonstrated that secondary explosions involving graphite dust are very difficult to initiate (using a methane-gas explosion as a primary driver), and that in a pipeline situation with an extremely energetic ignition source (major electrical discharge), the potential deflagration in a suspended graphite-dust cloud was self-extinguishing. The suitability of these experimental configurations to demonstrate this lack of an effect for graphite dust was validated in both cases by substituting reactive maize or wheat flour, which then produced significant deflagrations.
7. Classically, the following conditions must be satisfied *simultaneously* in order for a dust explosion to occur:

    a. The dust must be airborne;
    b. An ignition source of sufficient energy must be present;
    c. The dust must be combustible;
    d. The atmosphere must support combustion;
    e. The concentration must lie within the explosible range;
    f. The particle-size distribution must be optimized for flame propagation.

    To this may be added the additional condition that, for a disruptive explosion to result, there must be confinement. It is clear that, for graphite dust, condition (e) is especially difficult to achieve in a practical decommissioning situation, since particles greater than about 5 μm in diameter tend to act as heat sinks, whilst condition (b) is only attainable with difficulty since the material is only very weakly ‘explosible’. In any practical decommissioning situation, it is relatively easy to ensure that at least one of these conditions is not present.
8. It is therefore concluded that the ‘risk’ of a dust explosion involving graphite dust during reactor decommissioning is extremely low, and should not cause particular concern in planning a decommissioning strategy. It is, of course, prudent to eliminate *any* potential risk by eliminating one or more conditions from (7) in the course of designing the strategy

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A

THE ESTABLISHMENT AND PROPAGATION OF A FLAME FRONT IN A DUST SUSPENSION

A.1 Ignition

Whatever the ignition source, certain criteria must be fulfilled before a combustion wave can propagate through a flammable mixture of gas and dust. Firstly, an ignition volume must be established in the combustible media in which the rate of heat input from the ignition source is much greater than the rate of loss to the ambient mixture. The temperature then rapidly rises until that of ignition is attained and exceeded, thereby initiating the release of chemical energy.

The adjacent layer of combustible media heats up to ignition, and a flame front is established which then propagates outwards. For a deflagration to be sustained, the flame must have attained a certain width, corresponding to a steady-state combustion wave, in the time taken for the temperature of the initial volume to have fallen to that of the flame. This ensures that the temperature gradient between ignition volume and ambient gas is the same as that across a steady-state combustion wave (flame). If the width of the newly established flame is less than that of the steady state, then the temperature gradient will be too steep and heat loss to the surrounding cool gas will exceed that generated by chemical reaction within the flame and ignition volume. If this situation exists, the reacting volume then cools, reducing the chemical reaction rate, resulting in the ultimate expiration of the combustion wave.

The relative effectiveness of different ignition sources may now be assessed. Flame sources have a large ignition volume, ensuring smaller surface-area-to-volume ratio within it, lowering the heat loss rate relative to that of heat build-up within the volume, and are thus very efficient. Chemical igniters deliver a similar result. Electric sparks (including lightening strikes, which have been included in some existing safety assessments) have high power densities, and heat input to the ignition volume is virtually instantaneous, resulting in very high temperatures. A capacitive discharge is superior to an inductive discharge in this respect. In these cases, in addition to the thermal effect and the transport of radicals formed in the chemical reactions, ionization of the gaseous medium together with the surface electrical resistance of the particles are also significant parameters in determining the effectiveness of the ignition.

A.2 Flame Propagation

A.2.1 Input Parameters

The speed with which the combustion process, or flame front, can propagate depends upon the chemical reaction rate and the heat-transfer rate from the flame to the unburnt dust. In this context, 'chemical reaction rate' includes both the basic kinetic rate of reaction and also other relevant parameters such as the particle surface-area-to-volume ratio (size distribution), concentration, and temperature. Dust morphology is also important, especially where it changes during the combustion process. Coal dusts lose their volatile components which initially enhance the exothermic processes, other materials may vaporize, and more inert forms of carbon such as graphite act as both heat sinks and radiators, thereby diminishing the efficiency of the propagation. In such a material, the deflagration would have to be sustained by the energy released by reaction at the particle surfaces and maybe within its porosity if sufficient oxygen can penetrate. In all cases, but especially in the case of materials such as graphite, initially high temperatures and high surface-area-to-volume ratio in the particles (*i.e.* fine dusts) appear to be necessary pre-requisites. Finally, the chemical reaction rate will also be dependent upon the mass transfer of oxygen to the reacting surfaces: hence, the intensity and magnitude of turbulence in the gas may have a direct influence on the propagation of the flame front in addition to its role in initiating the dust suspension.

The flame front in a deflagration possesses a finite width which depends on the nature of the reactants and the gas dynamics. The width of a laminar *gas* flame can vary between 20 – 500 μm whilst that in a dust deflagration is 10^2 – 10^3 times greater.

A.2.2 Propagation Velocity

We now define some parameters relevant to velocities of propagation (see Figure A-1). A number of different relative velocities are needed in order to define the relative movements of flame front, shock wave and the reacting medium to a fixed datum:

The *flame velocity*, S_F:	velocity of the flame front relative to some fixed datum;
The *burning velocity*, S_u:	velocity of the flame front relative to the unburnt combustion medium[26];
The *displacement velocity*, S_D:	velocity of the unburnt combustible medium relative to some fixed datum,

whence $S_D = S_F - S_u$

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[26] This is the 'external' burning velocity (away from the particle surface): a second velocity of burning towards the centre of particles may also be defined).

The burning velocity is an important parameter which characterizes the rates of chemical heat generation and gas expansion. In the case of a *stationary* flame (such as a laboratory propane burner) the burning velocity is equal in magnitude to the displacement velocity, and the *hot burned gas velocity* S_B is of the same magnitude.

In modeling the process of a dust deflagration, it is mathematically convenient to set the velocity of a *propagating* flame to zero with appropriate adjustments to other velocities.

Taking a single dust particle, which is assumed to be spherical, the time taken for the radius to reduce by an amount *b* due to oxidation can be equated to the time required for the traverse of the flame across the same particle. Referring to Figure A.1, the time for the reduction in particle radius is:

$$\tau = \frac{v\rho_p}{a_p r'}$$

and the time of traverse is: $\tau = \frac{l}{S_B}$

whence $S_B = \frac{a_p r' l}{v\rho_p}$

But $S_B = S_F$ and $S_F =$ $S_u \frac{\rho_u}{\rho_B}$*;* hence $S_u = \frac{\rho_B a_p r' l}{\rho_u v \rho_p}$

Replacing $_p$ by $\frac{m_p}{v_p}$ gives $S_u = \frac{r' l \rho_B v_p}{} \rho_u v \frac{a_p}{m_p}$ where symbols are defined as follows:

r' = rate of combustion per unit surface area

l = flame width

a_p = surface area of particle

v_p = volume of particle

$_p$ = density of particle

m_p = mass of particle

v = volume of gasified graphite = $\frac{4}{3}\pi\left(R^3-(R-b)^3\right)$;

if b<<R then = $\frac{4}{3}\pi R^2 b$

R = radius of particle

b = depth of oxidation

$_B$ = density of hot burnt dust/gas mixture

$_u$ = density of cold unburnt dust/gas mixture

The expression for S_u shows that the burning velocity (laminar or turbulent) is directly proportional to the heterogeneous combustion (gasification) rate and the surface area to mass ratio of the particle. It is also dependent upon the concentration of the dust in the air. Heat and mass transfer to and from the particle determine the magnitude of the reaction rate. Turbulence, up to a certain level, increases heat and oxygen transfer beyond which heat removal from the flame becomes excessive and the deflagration is extinguished.

Two types of turbulence may be distinguished. These are gas-displacement turbulence, and flame-induced eddy generation. The first is turbulence generated by gas displacement in some constraining geometry, and produces a range of eddy sizes due to the progressive break-up of the largest of these. Maximum eddy size is of the order of the characteristic dimension of the constraining geometry (for example, pipe diameter). The minimum size which is limited statistically has a linear scale given by

$\sim \frac{d}{(R_e)^{\frac{3}{4}}}$ [A1] where = minimum linear scale of an eddy, d = maximum characteristic dimension (*e.g.* pipe diameter) and R_e = Reynolds number. As an example, in a 1 metre diameter pipe, with a Reynolds number of 10^4, = 10^3 μm. Large-scale eddies increase mixing and heat transfer between flame and unburnt gas by distortion of the combustion front, effectively increasing the width of the flame, but do not affect the oxygen transfer to the surface of the particles which continues by molecular diffusion. If, however, the scale of the eddy is comparable with the size of the particle, then eddy diffusion will increase the oxygen transport rate to the particle surface, and so increase the reaction rate. In this case, the boundary layer around the particle is effectively reduced. Molecular diffusion rates increase inversely with particle diameter. Essentially what this means is that smaller pipe diameters increase the potential risk and severity of any deflagration, provided that heat loss to the walls is not excessive and that the gas displacement velocity is sufficient to overcome any effects of drag.

Since , $R_e = S_g \frac{d}{\nu}$

the minimum linear scale can be written $\lambda = d^{1/4}\left(\frac{\eta}{S_g}\right)^{3/4}$

with *Sg* = gas speed and = kinematic viscosity. Therefore decreases in minimum scale are much smaller than those in pipe diameter and easily offset by increases in drag and thermal losses.

The second type of turbulence is that induced by the flame itself. This is significant only in freely-expanding spherical explosions (as approximated by the ISO test rig and similar devices) and is due to perturbations in the flame front resulting from local changes in burning velocity. This style of turbulence increases with the radius of the expanding flame front, but it is much smaller in scale than the first type and does not occur in pipes.

This turbulent burning velocity is related to the laminar velocity and the initial cloud radius by the following expression:

$$\frac{S_T}{S_L} = 1 + (E-1)\left[1 - \exp(-0.038 r_0)\right]^{1/2}$$

where E is the ratio of the gas density ahead of the front to that behind

$$(i.e.\ \frac{\rho_2}{\rho_1} = \frac{\rho_0}{\rho_1})$$

r_0 = initial radius of the cloud;

S_T = turbulent burning velocity; *and*

S_L = laminar burning velocity.

In some instances, laminar burning velocities are not known and the turbulent value cannot therefore be calculated without estimation.

A.2.3 Reaction Kinetics and Thermochemistry

The acceptance of boundary-layer controlled kinetics for steady-state graphite combustion in a deflagration effectively eliminates chemical kinetics as a controlling factor except at sub-micron particle sizes. Hence, any reactive non-graphitic carbon present should not result in a more severe deflagration under the same conditions, and catalysts would not be expected to influence the outcome either. Ignition sensitivity may be enhanced when, in the early stage of combustion, boundary payers have not formed around the particles and the oxygen concentration at the surface is essentially the same as that in the surrounding atmosphere.

The actual chemical reactions taking place, whose relative importance is a function of temperature, may also affect the development of the deflagration. With the high flame temperatures generally observed, CO is the principle product of combustion:

$2C + O_2 \bullet 2CO$ (H = -111 kJ.mol^{-1})

CO will of course undergo combustion through the reaction

$2CO + O_2 \bullet 2CO_2$ (H = -282 kJ.mol^{-1})

Therefore, a heterogeneous reaction is followed by a homogeneous one which produces the majority of the heat released. It has been observed that CO tends to burn close to the surface of large graphite masses when combustion is achieved at elevated temperatures in a plentiful supply of air[27] [A2]. For smaller masses the fraction of CO burnt in the vicinity of the reacting surface is much reduced and for particles less than about 50μm diameter the CO may be assumed to burn in the atmosphere between the particles. Despite depleting the oxygen concentration within the combustion zone, the more uniform heat distribution resulting from the homogeneous reaction is likely to enhance heat transfer to the cold gas and thus increase the propensity towards deflagration of a cloud of smaller particles.

There is an additional feature in the combustion of many dusts which is absent in the case of graphite. This is the release of gaseous combustible substances upon heating. For coal dust, for example, the release of volatiles provides further readily combustible material which ignites homogeneously and provides much of the energy to drive the reaction.

The burning kinetics of carbonaceous particles in general have been extensively modeled by a number of groups. The importance of particle size in particular has been commented upon extensively in this review, with only the smallest particles appearing to participate significantly in any dust deflagration for graphite and the internal (and external) heat conduction being considered critical. Possible explanations for this have been given and include the possibility of the thermal conductivity allowing movement of heat away from the oxidizing surface into the depths of larger particles [A3], thus inhibiting the oxidation somewhat by reducing the surface temperature.

Whilst the classical equations in this Appendix might be modified to accommodate such effects, it is considered more useful to refer the reader to modern comprehensive computer simulation techniques which have been developed explicitly for such scenarios. The present authors prefer and recommend the Carbon Burnout Kinetics Code (CBK8) developed by Brown University, RI, USA [A4]. The most recent version of this code is discussed in detail in [A5], an article which concentrates explicitly on the issue of extinction of combustion.

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[27] i.e. when the ‘Schweitzer conditions’ defined in [1] are met

In this model the single particle combustion rate is modeled with the following equation:

$$R = \eta k_0 S_0 P_{ox}^{n} m_p \exp\left(-\frac{E}{RT_p}\right)$$

where R is the particle combustion rate,   is dimensionless effectiveness factor (near unity for Mode I oxidation whilst lower values indicate Mode II conditions under which the oxygen penetration depth is much less that the particle radius and thus the observed oxidation rates are much less than the intrinsic rates at the given temperature), k_0 is the pre-exponential factor for the surface rate constant in grams carbon.s^{-1}.cm^{-2}.atm^{-n}), S_0 is the specific surface area of the particle (cm^{2}.g^{-1}), P_{ox} is the oxygen partial pressure at the particle reacting surface, n is the empirical apparent reaction order with respect to oxygen for the range of T and P being examined, m_p is the carbon mass in the particle and T_p its temperature.

In this form there is no explicit allowance for thermal conductivity values to be input, and this aspect could perhaps be examined in further work. However, the results of work undertaken in support of the UK Windscale Piles decommissioning program in terms of particle-size effects are worthy of comment. Calculations were undertaken for particles of 1, 10 and 20 μm diameter with additional allowances for particle porosity (the original model was intended for essentially non-porous coal); the results found that the maximum burnout under good combustion conditions (high temperature, 2173K, and atmospheric oxygen concentration) was only 12, 14 and 15% for 1, 10 and 20 μm particles respectively after 10 ms, with very little change in particle size overall, a result described (in 'burning' terms) as 'poor'. This result taken in isolation does not therefore explain the apparent participation in combustion of only the smallest graphite particles, as proposed by the work at The University of Leeds, UK. However, the modeling contained a number of assumptions and could be extended to accommodate more complex thermal hydraulic conditions, as suggested above, if deemed to be necessary to support the experimental observations.

A.3 Calculation of Explosion Pressure

Explosion pressures for a graphite-dust deflagration may be estimated using what is known as the 'acoustic solution' of the equations of fluid motion describing the flow field outside the flame front [A6, A7]. A necessary condition is that the flame velocity is much less than the velocity of sound, and this is demonstrably the case for a graphite deflagration. Spherical geometry is assumed (as in the ISO standard test and in similar vessels) with central ignition of the dust suspension.

Heat released by the combustion raises the pressure and temperature of the mass of the reaction products inside the spherical flame front to constant maximum values until the flammable mixture is exhausted.

The explosion pressure decreases with radial distance as shown in Figure A-2. The acoustic solution utilizes a mechanical model to simulate the thermochemical effects of combustion (Figure A-3). A spherical piston expands and compresses an amount of gas equivalent to that within the boundary of the flame front, such that the same maximum pressure and flow-field pressure distribution are generated. The leading edge of the flow field advances at the velocity of sound in the ambient atmosphere. As this is much greater than the piston (or flame) velocity, the flow field expands with time although the maximum pressure within the flame front is constant.

The assumption of a flame velocity small (less than one half) in comparison with the velocity of sound implies that the gauge pressure at any position in front of or behind the flame front is small compared with the ambient atmospheric pressure. Hence, adiabatic heating effects on the air in front of the flame are small, producing commensurate changes in the local velocity of sound which, in the developed theory, is assumed to be the value in the surrounding atmosphere. Also, the use of the same expression to calculate the excess pressures for both gas and dust explosions is justified on the basis that the principal differences between the two are manifested in the burning velocity, which is obtained separately as previously described.

The excess pressure ('explosion pressure') above that of the atmosphere for an unconfined explosion is given by the following expression:

$$P - P_0 = \frac{2\rho_0 a_0{}^2 M_p{}^3}{\left(1 - M_p{}^2\right)} \left(\frac{a_0 t}{r} - 1 \right)$$

where P = total explosion pressure at radial distance r and time t;

P_0 = atmospheric pressure;

$_0$ = density of the atmosphere (air);

a_0 = velocity of sound in the atmosphere;

r = radial distance from the centre of the explosion

$(0 < r < a_0 t)$; *and*

M_p = spherical piston Mach number.

At the flame front, $r = r_f$ and $r_f/\ t$ is the flame velocity which gives the maximum explosion pressure. The relationships between the piston Mach number and the flame and burning velocities are given by

$$M_f = \frac{\rho_1}{\rho_2} M_{su} \qquad \text{and} \qquad M_p = M_f \left(1 - \frac{\rho_2}{\rho_1}\right)^{\frac{1}{3}}$$

where $_1$ = density of the unburnt mixture ahead of the flame front;

$_2$ = density of the combustion products inside the flame front;

M_f = flame velocity Mach number; *and*

M_{su} = burning velocity Mach number.

It is assumed that $_1 = {}_0$, hence $\frac{\rho_1}{\rho_2} = \frac{\rho_0}{\rho_2} - \frac{T_2}{T_0}$

where T_0 = temperature of the ambient atmosphere *and*

T_2 = temperature of the combustion products, *i.e.* flame temperature.

The rate of pressure rise with respect to radial distance is a maximum at the flame front, as is the rate with respect to time. For a fixed radial distance, the temporal rate of pressure rise is a constant. This is a consequence of the stretching of the flow field. The rate of pressure rise with respect to time is given by the derivative of the expression given earlier for $P - P_0$:

$$\left(\frac{\partial P}{\partial t}\right)_r = \frac{2\rho_0 a_0{}^3 M_p{}^3}{r\left(1 - M_p{}^2\right)}$$

These two expressions may be used to obtain order of magnitude estimates of $P - P_0$ and $P/\ t$ at the maximum radial distance traveled by the flame front before being extinguished – *i.e.* the total combustion of the flammable suspension up to $r = R_F$.

Due to thermal expansion of the reaction products, the unburned mixture ahead of the flame and the surrounding air will be displaced. The initial diameter of the flammable mixture will therefore increase to a maximum value at complete reaction, which is given by

$$R_F = r_0 \left(\frac{\rho_0}{\rho_2}\right)^{\frac{1}{3}}$$

Where R_F = maximum radius of the flame front attained for complete reaction of the flammable mixture *and*

r_0 = initial radius of the flammable suspension at $t = 0$.

Literature values for some of the parameters involved in these equations are extremely difficult to find for the graphite dust situation, hence requiring reliance on appropriate experiments to obtain suitable data.

A.4 References to Appendix A

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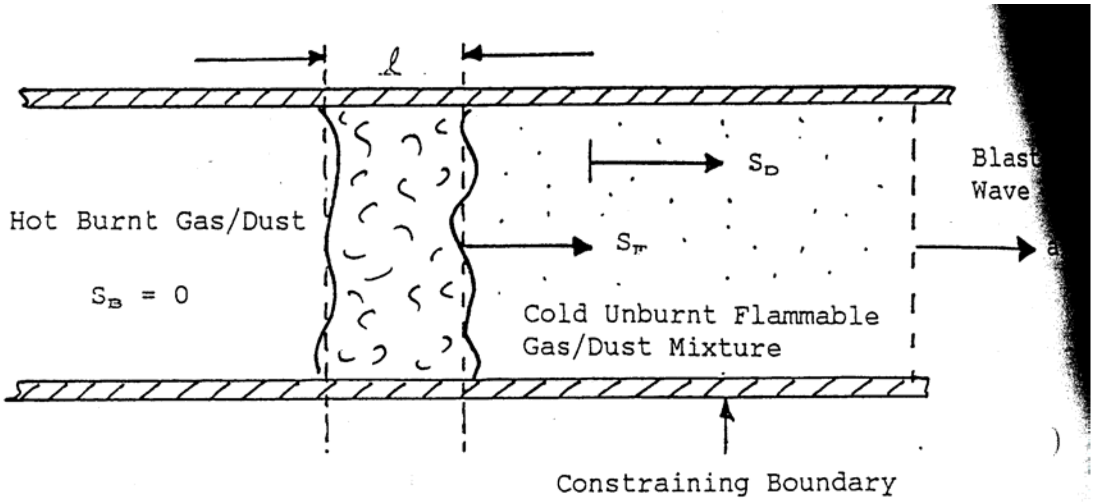

S_B = Bulk velocity of hot combustion products

= zero for:

a partially confined explosions in a pipe/channel open at one end ignition at closed end

b partially confined explosions in a pipe/channel open at both ends- ignition in central region

c unconfined explosions

> zero for: partially confined explosions in a pipe/channel open at one end - ignition at open end

ℓ = mean flame width

a_o = velocity of blast wave

= velocity of sound

Figure A-1
Schematic Representation of a Partially-Confined Dust Deflagration

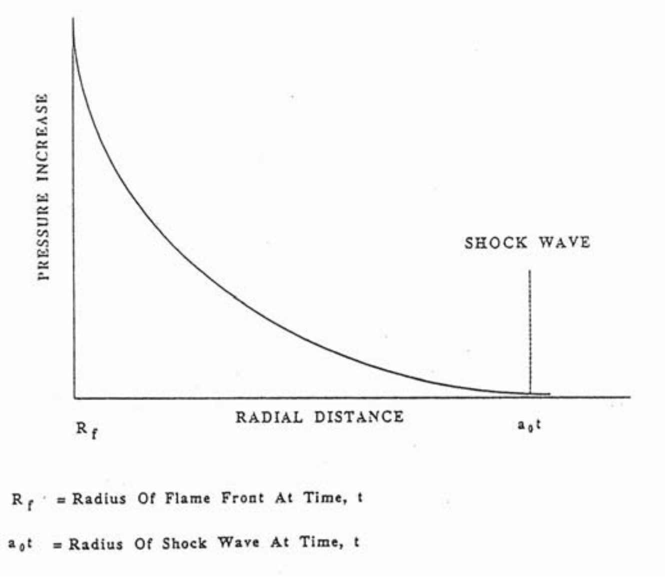

Figure A-2
Pressure Distribution in an Unconfined Explosion Given by the Acoustic Approximation

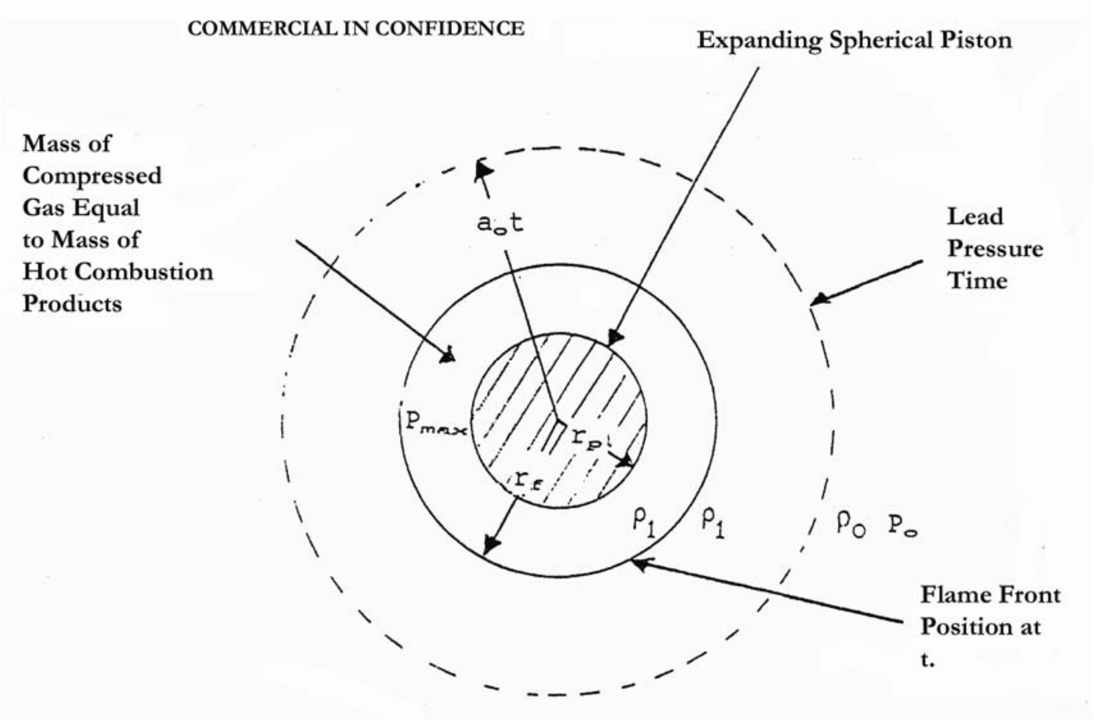

Figure A-3
Mechanical Model of an Unconfined Deflagration incorporating an Expanding Spherical Piston

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