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ABSTRACT

The hazards associated with the use of magnesium capsules in a CO₂-cooled reactor system have been analyzed and consideration has been given to incidents which could lead to excessive temperature excursions and factors which could significantly reduce the ignition temperature of magnesium alloys. Methods of reducing the hazards associated with the Calder Hall type of reactor are discussed, and an experimental approach with which to more accurately define conditions that would lead to ignition is suggested.

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AN ANALYSIS OF THE MAGNESIUM-CO₂ REACTION IN TERMS
OF A REACTOR ENVIRONMENT

J. L. Scott

The fuel element cladding in a Calder Hall type of reactor is a Magnox alloy consisting of approximately 0.05% Be, 1% Al, other minor constituents, and the balance Mg. The reactor coolant is CO₂, and under normal operating conditions the peak temperature of the Magnox cladding is held down to 400°C. It was the purpose of the study reported here to examine the conditions which might lead to ignition of the magnesium in the CO₂, to examine factors which affect the ignition process, and to specify areas in which the acquisition of additional information might lead to reduction of the fire hazard. The following discussion and the conclusions reached are based on the data which could be found and the limited analysis of that data which could be made in the short period allotted for the study and the preparation of this report.

Although there is a strong driving force for Mg and CO₂ to react at lower temperatures, the ignition temperatures of bulk magnesium and Magnox in CO₂ are above 600°C.¹ Thus if it is assumed that in a Calder Hall type of reactor no event can occur that will cause leakage of air into the system or pulverizing of the fuel element cladding, the fire hazard is related only to events which could increase the temperature of the fuel element cladding to the ignition point or to contaminants in the CO₂ or cladding or other factors which could lower the ignition temperature.

Incidents Which Could Raise Reactor Temperatures

Cooling System Failures. The cooling of the surfaces of the fuel elements could be stopped or seriously reduced by plugging of a channel caused by the chipping off of a large piece of graphite or by warpage of a fuel element. A large leak in the pressure vessel, the failure of blowers, or malfunctioning of the large valves in the coolant ducts could also cause loss of cooling. Even if the reactor were scrammed upon the discovery of loss of cooling, the afterheat might produce a large enough temperature rise to cause ignition of the cladding of the fuel elements.

Nuclear Power Transients. Improper control of the reactor could increase the power output and thus increase the temperature of the coolant and fuel element cladding to the ignition point. A detailed analysis of transients in a gas-cooled reactor has been made by the staff of ORNL.²

Release of Wigner Energy. Radiation causes energy to be stored in graphite, probably in the form of vacancies, interstitials, and severed bonds in the graphite lattice. When this stored Wigner energy is released, by controlled annealing or by accident, heat is produced in the graphite. The amount of stored energy decreases with increased reactor operating temperatures, and therefore the frequency with which controlled annealing must be carried out will be less for a Calder Hall type of power reactor than for a plutonium production reactor. If, however, the temperature of the graphite were raised sufficiently during power operation because of a nuclear power transient or loss of cooling to bring about release of the Wigner energy, the ambient temperature might become sufficient to ignite the magnesium cladding.

Effect of Reactor Conditions on Ignition Temperature

Oxidation Reaction. The ignition temperature of a metal in an oxidizing atmosphere is the lowest ambient temperature at which the oxidation reaction will proceed rapidly enough to cause a rapid temperature increase at the gas-metal interface. Methods by which the heat produced by oxidation of a metal can be dissipated and ignition prevented are (1) conduction of heat away from the interface by the metal and (2) removing the heat by convection or radiation. Thus, any factors which affect the rate of heat generation, i.e., the rate of oxidation and the rate of heat dissipation, affect the ignition temperature. It is well known that fine particles of an oxidizable material ignite at a lower temperature than do bulk samples. Fine powders of magnesium can ignite in air at room temperature and great care must be exercised in handling the materials. In contrast, bulk samples of magnesium do not ignite in pure oxygen until a temperature of 623°C is reached.³ The ignition temperature of bulk magnesium is not determined primarily by the oxidizing potential of the gas; it ignites in steam at 630°C ⁴ and in CO_2 at 642°C .⁵ Since the combustion of magnesium occurs by a vaporization process, the narrow range of the ignition temperatures in different oxidizing agents is not unexpected. A theoretical analysis of the relation between particle size and ignition temperature for zirconium has been given by W. R. DeHollander.⁶ His analysis showed a positive linear correlation between $1/d$ and $1/T$, where d is the particle diameter and T is the absolute temperature.

The ignition temperature is also quite dependent on the type of oxide film which is formed. Littman and Church,⁷ for instance, have shown that zirconium and titanium ignite at room temperature in oxygen at 2000 psi when samples are ruptured. Under the same conditions Mg, Al, Ta, Cb, Mo, Fe, and stainless steel do not react. The differences were interpreted to be due to the higher solubility of the oxide in titanium and zirconium and the consequent prevention of the formation of a protective oxide film. In air, Magnox C (1% Al, 0.05% Be, bal Mg) does not ignite even when ruptured at 400°C.⁸ Data on the effect of rupture for pure magnesium and Magnox C at higher temperatures are lacking.

Effect of Alloying Additions. Alloying additions to magnesium usually impair the oxidation resistance and thus lower the ignition temperature. Leontis and Rhines⁹ reported that nickel and copper are most effective in accelerating the oxidation rate, the elements Fe, Ag, In, Mn, Ca, Si, and Nb have only a minor influence, and Ce and La materially reduce the rate. The ignition temperature may also be lowered by alloy additions resulting from the interdiffusion of different metals and magnesium. Fassel et al.¹⁰ found that the ignition temperature could be lowered by contacting magnesium with certain metals (see Table I). Fassel also found that the reduction in ignition temperature caused by alloying the magnesium with aluminum could be correlated with the melting points of the alloys.

The most striking effect of alloying additions on the ignition temperature is the increase in ignition temperature produced by beryllium

TABLE I¹⁰

THE LOWERING OF THE IGNITION TEMPERATURE OF MAGNESIUM
IN CONTACT WITH OTHER METALS IN OXYGEN

<u>Contact Metal</u>	<u>Ignition Temperature (°C)</u>
Magnesium	623
Silver	623
Steel	623
Nickel	588
70 - 30 Brass	538
Aluminum	523

additions of up to 0.05%. Huddle and Wyatt¹¹ have reported that by such additions the ignition temperature of magnesium in air may be increased to a value above the melting point of the alloy. Calcium was also found to raise the ignition temperature, but such additions make the resulting alloys difficult to fabricate. To facilitate the addition of beryllium to magnesium, aluminum (1%) is added to produce the Magnox alloys.¹² Although the mechanism by which beryllium increases the ignition temperature of magnesium is not known, it would be expected to be due to a change in the characteristics of the oxide film.

Effect of Impurities in CO₂. Impurities in the gaseous reactant may also affect the ignition temperature of a metal. Moisture in CO₂ for instance increases the rate of attack on magnesium at elevated temperatures.¹³ In impure CO₂ the reaction is characterized by relatively rapid attack that spreads from points on the surface and produces an effect similar to pit corrosion in aqueous media. In pure magnesium this attack was observed at 550°C. When Magnox E (0.05% Be, 0.1% Ca, 1% Al) was tested in moist CO₂, no failure occurred in 2500 hr at 615°C. A minimum of 0.02% Be and 0.07% Ca were found to give immunity from breakdown in moist air at 600°C. The effect of impurities in the gas on the oxidation rate is undoubtedly the result of a change in the nature of the oxide film formed.

Hydrodynamic Factors. Pressure and flow rate of the gaseous reactant also affect the ignition temperature of the metal. In general, the effect cannot be predicted, because increased pressure and flow rate serve at the

same time to increase the rate at which gas molecules are supplied to the reaction interface and the rate of cooling of the interface. Although the LeChatelier principle would say that the rate of reaction between magnesium and oxygen should increase with increasing pressure, the ignition temperature of magnesium in O_2 has been reported to increase from 623°C to 643°C as the pressure is raised from 1 to 10 atmospheres.¹⁰ Contradictory evidence has been given by Baur *et al.*,¹³ who report an ignition temperature of 591°C for magnesium in 7 atmospheres of oxygen. The discrepancy is attributable to differences in the impurities in the alloys, differences in surface preparation, or differences in the purity of the oxygen. In general, the ignition temperature for the Magnox- CO_2 reaction increases with increasing CO_2 flow rate.⁸

Possible Effects of Calder Hall Reactor Conditions. From the above discussion it is clear that the ignition temperature of the fuel canning material used in the Calder Hall type of reactor could be lowered by the introduction of impurities in the gas. For example, water vapor could be introduced into the CO_2 if the steam heat exchanger developed a leak, and other impurities could exist if the reactor had not been properly purged during startup. Furthermore, the ignition temperature might be lowered to about 500°C , if metallic contaminants, such as copper or aluminum, were inadvertently introduced (see Table I). This would occur only if the

effect of alloying on the ignition temperature in CO_2 is similar to the effect in oxygen. Although the production of a fresh surface does not appear to appreciably lower the ignition temperature of magnesium, there exists the possibility that the ignition temperature would be reduced by rupture of a fuel element can. Since the ignition temperature is a function of the nature of the oxide film and radiation is known to impair the properties of films, radiation damage might also lower the ignition temperature of magnesium and magnesium alloys.

Effect of Melting of Cladding or Fuel. The possibility of ignition of the cladding or the fuel material due to melting of the cladding must also be considered. Although bulk Magnox, which will probably be used as the fuel canning material for future Calder Hall reactors, does not ignite even above the melting point (645°C) in air, a fire could be initiated by melting if some mechanism existed for the dispersion of the molten metal into fine particles. Such a dispersion could be produced, for example, by the dripping of molten Magnox into flowing CO_2 . Since, as Huddle¹⁴ has indicated, uranium metal does not ignite in CO_2 at temperatures up to 750°C , a fire due to the reaction of CO_2 with uranium per se would not be expected. It is conceivable, however, that the ignition temperature of uranium in CO_2 would be adversely affected by radiation damage.

Methods of Preventing the Occurrence of a Fire

Provision of Sufficient Instrumentation. The most obvious method of preventing a fire in a Calder Hall type of reactor is to provide sufficient

instrumentation to ensure that the reactor is shut down long before the ignition temperature is reached. This is the approach taken by the British at Calder Hall. The intricate instrumentation provided has been described by Anderson and Bowen.¹⁵ With this instrumentation, only a complex, unlikely sequence of simultaneous failures could lead to a hazardous condition.

The British feel that the Windscale type of accident could not occur at Calder Hall for the following reasons:¹⁶

1. Annealing to release the stored Wigner energy will be required less frequently because the minimum temperature of the graphite is higher.

2. Wigner energy release can be conducted under fully controlled conditions and will not be hazardous, since in the CO₂ coolant, in contrast to air, higher temperatures (750°C) are required to ignite uranium, and thus a greater safety margin exists. The closed coolant circuit at Calder Hall also permits better control of temperatures. Further, the Windscale scanning gear was movable, and it jammed at high temperatures during the "incident"; the Calder Hall detection equipment is fixed and provides for monitoring each fuel channel continuously. In addition, the fuel capsules at Calder Hall have exhibited a much lower failure rate and a low corrosion rate. The instrumentation and controls for regulating the rate of power change in Calder Hall reactors are much improved over those used at Windscale.

3. At Calder Hall the graphite is being continuously checked for the rate of storage of Wigner energy.

4. A leak in a fuel cartridge would be quickly detected and brought under control before serious oxidation of the uranium and spread of the

fission products could occur. Any fission products that were released would be retained in the closed coolant system.

Addition of Helium to CO₂. A second method of reducing the hazards associated with the Calder Hall type of system might be to reduce the oxidizing ability of the gaseous atmosphere by replacing a portion of the CO₂ with helium. This method is unlikely to be effective, however, unless relatively high percentages of helium are used, because the CO₂ could be expected to be preferentially chemisorbed on the surface of the magnesium and thus the localized CO₂ concentration would be increased to above what would be expected from ideal theory.

The effects of helium additions on the heat transfer properties of the He-CO₂ mixtures must also be considered. In making any meaningful comparison between the heat transfer performance of pure CO₂ and of He-CO₂ mixtures, it is necessary to specify certain system parameters as being fixed, whichever coolant is used. In the present situation, logical choices for these fixed factors are system size and geometry, maximum coolant pressure, coolant temperature rise, and maximum fuel element temperature. The manner of specifying the flow rate of the coolant is not so obvious, however. Two possibilities will be discussed here: (1) maintaining the volumetric flow rate constant and (2) maintaining the pumping power constant.

For a system in which the size and speed of the coolant circulating blower could not be easily increased, the maximum volumetric flow rate would be a fixed factor. Under such a limitation, it can be shown that

CO_2 is superior to He- CO_2 mixtures as a heat transfer medium, primarily because of its higher volumetric heat capacity. The total heat transferred would decrease as the helium concentration was increased if the volumetric flow rate were held constant.

A similar analysis can also be made for the case of a constant pumping power. This would require an increased flow rate of coolant as the helium concentration was increased, and consequently an increase in blower size or speed would be required. Under these conditions, the heat transfer rate for the mixed coolant would still be less than that for pure CO_2 , except at very high helium concentrations. The rate of heat transfer provided by pure helium is approximately 5% greater than that provided by pure CO_2 .

In general, the addition of small amounts of He to CO_2 would appear to be ineffective in raising the ignition temperatures of magnesium under the conditions found in a Calder Hall reactor. The rate-determining step under these conditions appears to be activation of the magnesium. By analogy with the ignition of other metals by oxygen, 10% CO_2 in He is probably adequate to cause ignition of magnesium at a temperature close to the ignition point for pure CO_2 .

Replacement of Magnesium with Oxidation-Resistant Material. A third method of reducing the hazards associated with the Calder Hall type of reactor would be to replace the magnesium with a more oxidation-resistant material. The relative merits of other casing materials have been thoroughly considered.¹⁷ In general, it appears that such a change would require the complete redesigning of the reactor.

Suggested Experimental Studies

Two temperature regions may be used in studying the combustion process. At low temperatures, the rate of reaction is governed by the kinetics of the reaction. Beyond a certain critical temperature, i.e., the ignition temperature, the rate of reaction is so high that the rate of combustion is governed by the diffusional processes associated with the transport of reactants and products to and away from the reaction interface and is completely independent of the nature of the reaction. In order to thoroughly understand the combustion process, a study must be made of the mechanisms and kinetics of the process in both the kinetic and the diffusional regions and of the factors which determine the ignition temperature. In addition the interrelationships between the kinetics of the process and the ignition temperature must be determined. Since, in general, these interrelationships are very complex, the ignition temperature of a metal cannot be predicted from data on the kinetics of the oxidation process at temperatures in the kinetic region and empirical correlations of experimental data must be used. We have as yet been able to locate very little published data on the magnesium- CO_2 reaction. Therefore, in order to make quantitative predictions, a comprehensive program might have to be initiated which would involve the studies described below.

Kinetic Region of Combustion Process. Measurements of the weight gain of magnesium and magnesium alloy samples in CO_2 under a variety of conditions should be made at a series of temperatures as a function of time. Typical

conditions which should be varied are:

1. Nature of the surface, particularly when it is freshly formed.
2. Impurities in the gas, such as CO, H₂O, and air.
3. Alloy content of the magnesium.
4. Pressure of the gas.
5. Flow rate of the gas.
6. Helium content of the gas.
7. Specimen geometry and size.
8. Radiation field.

At each temperature and for each alloy under a given set of conditions, data would be obtained which would fit an equation of the type

$$W = k t^n + B ,$$

where

W = weight gain, g/cm² ,

t = time, sec ,

k, n, B = empirical constants.

The temperature effect is associated with the constant k , which would be expected to fit an equation of the type

$$k = k_0 e^{-Q/RT} ,$$

where k_0 is a constant, Q is the activation energy for the oxidation process, R is the gas constant, T is the absolute temperature. If sufficient data

were obtained to evaluate the constants in the above equations, the behavior of the process in the kinetic region would be specified.

In addition to weight gain studies, a complete program of investigation of the reaction process in the kinetic range should include electron microscope studies of the nature of the oxide films formed and a thorough evaluation of the types of reaction products formed when various alloying additions are made and when the gaseous impurities are varied.

Ignition Temperature. The complex factors which govern behavior in the kinetic range are also important in fixing the ignition temperature. The effect of each of these factors on the ignition temperature should be evaluated quantitatively and the interrelationships between the various factors should be determined. These data should then be correlated with the data describing the kinetic region.

The effects of melting on the ignition temperature should also be considered, since, with the Magnox alloys, ignition does not occur before melting. The rate of reaction of liquid Magnox in CO_2 should be investigated as a function of the metal temperature, the degree of dispersion, the gas flow rate, and other similar variables.

Diffusional Range Investigations. Studies should be made to determine the rate of combustion of magnesium and magnesium alloys in CO_2 after ignition occurs. Such important variables as the CO_2 pressure, the gas flow rate, the sample size, i.e., the ratio of sample surface to volume of sample, and gaseous impurity content should be investigated. The objective

of such experiments would be to determine the conditions necessary to quench a fire after it had once been initiated.

Additional studies would have to be made to evaluate the probability of a temperature excursion into the unsafe temperature range. Final testing should consist of extensive in-pile tests designed to simulate both likely and unlikely temperature excursions and environmental conditions which might be encountered in a reactor.

Summary and Conclusions

The hazards associated with the use of magnesium capsules in a CO₂-cooled reactor system have been analyzed and consideration has been given to incidents which could lead to excessive temperature excursions and factors which could significantly reduce the ignition temperature of magnesium alloys. Methods of reducing the hazards associated with the Calder Hall type of reactor are discussed, and an experimental approach with which to more accurately define conditions that would lead to ignition is suggested.

The following conclusions were drawn:

1. The possibility exists that an incident could occur which would result in a rapid reaction between the CO₂ and the magnesium fuel element cladding in a Calder Hall type of reactor, and the initiation of such a reaction would be likely to have extremely adverse effects.

2. The probability of an incident occurring that would cause ignition of the magnesium in a Calder Hall type of reactor operated under the British control system appears to be very low.

3. With proper contaminants the ignition temperature of the magnesium capsule could possibly be lowered to a value in the neighborhood of 500°C .

4. Any event which would produce melting of the magnesium fuel element cans would be a very hazardous occurrence.

5. It appears that He-CO_2 mixtures containing above 90% He would be required to reduce the hazards to a major degree.

6. An extensive in-pile study in which the actual reactor environment could be simulated would be required to give a precise knowledge of the hazards associated with the Mg-CO_2 reaction.

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