

APPENDIX 1

RADIOLYTIC OXIDATION IN GRAPHITE

Outline of gas-phase processes

The oxidation of graphite in radiolysed CO₂-based gas mixtures proceeds by a fundamentally different mechanism from thermal oxidation, and an understanding of the oxidation process requires some insight into the chemistry occurring in the gas phase. This section reviews the effect of irradiation on CO₂ and considers the effects of other species - CO, CH₄ and H₂O, maintained in the coolant of Magnox and AGR reactors.

Gaseous CO₂ is apparently stable under radiolysis, except at very high dose rates. Studies of isotope exchange between CO and CO₂ in gas mixtures, however, show clearly that this apparent stability is in fact the result of a dynamic process of decomposition and recombination; ionising radiation forms ion pairs in CO₂ which quickly interact to reform stable CO₂. The rate of formation of species under radiolysis is usually defined by the so-called G-value, the number of species produced per 100 eV of energy deposited. The G-value may vary with the nature of the radiation because the density of the ionisation produced can vary the probability of the fast recombination of the ion pairs. Values observed by various investigators are shown in Table AI.1, and vary between about 1 and 3. As noted by Wright and illustrated in Fig A1.1, the G-values bear a monotonic relation to the particle velocities.

TABLE AI.1

G-VALUES FOR VARIOUS IRRADIATING PARTICLES IN CO₂

Particle	<i>G</i> (ion pair)	Ref.
Electrons 18 keV	3.05	Jesse and Sadauskis (1955)
67 keV	3.04	
Protons 1.83 MeV	2.91	Larson (1958)
α-particles (Po ²¹⁰)	2.94	Widder and Huber (1958)
Recoil ions Th C 117 keV	0.98	Stone and Cochran (1957)
Th C 168 keV	1.01	
C ¹³ 1.64-2.92 MeV	2.38	Leake (1967)
O ¹⁶ and C ¹² 0.1-1.5 MeV	1.47-2.56	
O ¹⁶ 30 keV	1.45	Boring and Woods (1968)
40 keV	1.52	
50 keV	1.58	

This variation is not a significant difficulty in interpreting data from AGR or Magnox reactors, because in each case the energy deposition is largely due to energetic photons, with a rather smaller component from neutron scattering.

The situation is, however, complicated by the fact that most of the oxidation in graphite is due to species activated in the open porosity; and in order to estimate the number of active species produced it is necessary to estimate the rate of energy deposition in the pores of the graphite. Whilst the rate of energy deposition may be straightforwardly estimated by calorimetry, the values thus obtained are not necessarily those appropriate to the graphite pores.

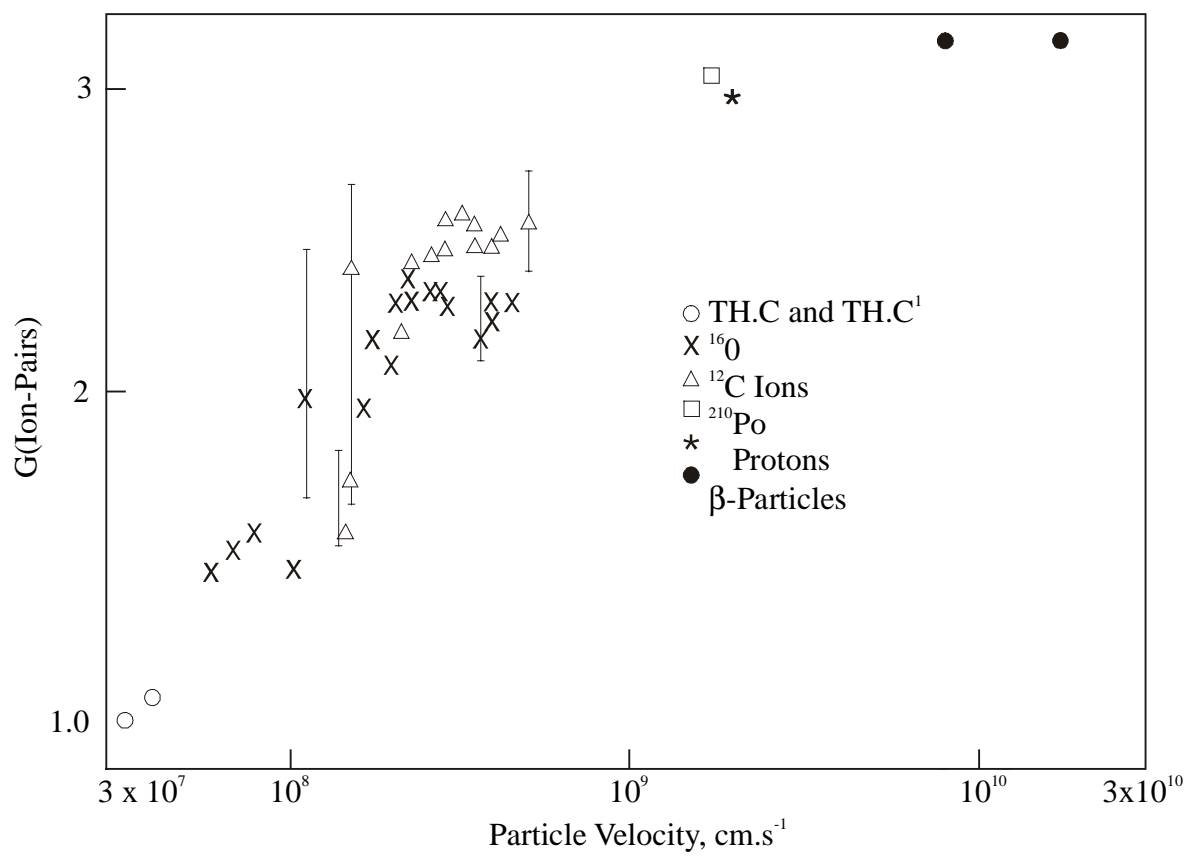


Figure A1.1 Variation in ion-pair yield in CO_2 with particle velocity

Given that a significant amount of the radiation yield is likely to be caused by secondary particles, if the volume of the pore is sufficiently small to allow some of the secondary particles to leave the pore unstopped the G-value will be modified. However, Linacre *et al* (1965) have concluded that for the spectrum of gamma energies found in reactors the pore sizes are large compared with the range of secondary particles, and that the gamma dose rates are close to those predicted by calorimetry. However, Wright has pointed out that for neutrons with energies up to 2 MeV this is not necessarily true for the recoil ions produced by neutron scattering. Nevertheless practical experience strongly suggests that taking the dose rate determined by calorimetry and using a G-value of 3 describes radiolysis of CO₂ in graphite pores satisfactorily.

The exact nature of the active species responsible for graphite oxidation has been extensively studied, but no firm conclusions have yet been reached. Most recent workers consider charged particles to be responsible rather than neutral species, but these ions could be more complex than the direct products of irradiation.

Mass spectrometer studies at the University of Liverpool, reported by Wood (1982), appear to indicate that clustered positive ions of the form [CO₂]^{+_n} are the primary oxidising species. These experiments also produced data on the effect of CO, which have been interpreted by Wickham *et al* (1977) to indicate the successive replacement of CO₂ units in the ionic clusters by CO. Similarly, in the presence of small amounts of water replacement by H₂O is possible (Wickham, 1979). Thermodynamic studies reported by Wickham and Headley (1983) strongly suggest that over most of the temperature ranges encountered in Magnox and AGR stations, the dominant positively charged species should be [CO₂]^{+₂}. However, the effect of CO on this species should be to produce [CO]^{+₂}, which is not capable of oxidising graphite. Similar difficulties are encountered if one considers the trimer [CO₂]^{+₃}. There is therefore some doubt as to the efficacy of positive ions in the graphite oxidation process.

The negative ion chemistry leads primarily to the formation of the CO₃⁻ ion. Whilst there has been some debate on whether the rate of reaction between this ion and CO is sufficiently fast to account for the observed inhibition by CO, recent studies on the range of active species have gone some way to resurrecting the possibility. Experimental data on negative ion clusters is poor, but estimates indicate that CO₃⁻ is likely to be important under most reactor conditions, although some doubt has been cast on this conclusion by Kummeler *et al* (1977).

In the presence of methane the chemistry occurring in the gas-phase is considerably more complex, and the reader is referred to a paper by Norfolk *et al* (1983) for a fuller description than is possible or appropriate here. Essentially, however, CH₄ molecules react with activated CO₂ species, resulting in deactivation of the CO₂, with formation of radicals and ions from the CH₄, which may react with each other or with CO₂ or CO to form more complex organic species. Some of the reaction products migrate to, and interact with, the walls of the graphite pore.

The implications of gas-phase chemistry for graphite oxidation

As noted above, the nature of the oxidising species is still a matter of some debate, but whatever its nature it may suffer one of three possible fates:

- (i) It may be deactivated by collision with CO₂ in the gas-phase.
- (ii) It may be deactivated by collision with CO or CH₄ (or perhaps by collision with some other hydrocarbon species formed radiolytically from CH₄).

(iii) It may reach the pore walls and gasify a carbon atom, producing CO.

Graphite oxidation rates are therefore determined not only by the number of active species produced, but also by the distance they diffuse without being deactivated and hence the probability that they will reach the graphite surface. Johnson (1981) quotes an expression for mean diffusion length for the active species in terms of the diffusion coefficient, D , and the CO and CH₄ concentrations, $[CO]$ and $[CH_4]$:

$$L = \frac{\Delta}{k_1[CO] + k_2[CH_4]}^{\frac{1}{2}} \quad (\text{A1.1})$$

Experimental evidence suggests that the effectiveness of CH₄ as a gas-phase inhibitor is some 10 times greater than that of CO for equal concentrations. These mechanisms for deactivating activated CO₂ species will reduce the rate of carbon gasification substantially below that expected in pure CO₂, and give rise to what is generally termed ‘gas-phase inhibition’.

As noted above, some of the products of CH₄ radiolysis may migrate to the surface of the pore wall. These species act to reduce the rate of graphite oxidation, although the mechanism is unclear. There are two main possibilities: either they act by blocking the access of oxidising species to active sites on the graphite surface, thus preventing carbon gasification; or they form a sacrificial layer on the graphite surface which is oxidised preferentially, thus preserving the carbon substrate.

The rate of radiolytic oxidation of a graphite specimen will therefore be affected by the number of active species produced in the gas-phase, the fraction of these species reaching the graphite surface and gasifying carbon atoms, and the effects of surface protection mechanisms. The distance travelled by the active species before being deactivated by collision in the gas-phase is small; this means that the vast majority of the radiolytic oxidation occurs in-pore, as almost all the active species produced in the bulk gas are deactivated before reaching the graphite surface, and only the production of active species within the graphite porosity need be considered. The porous structure of the graphite will therefore be an important determinant of the oxidation rate. The relationship between porous structure and oxidation rate is complex, and is best approached by considering first the situation where all inhibition of the oxidation reaction takes place in the gas phase, and then extending the treatment to the situation where surface inhibition is also significant.

Gas-phase inhibition only

Consider the effects of porous structure in the situation where only gas-phase inhibition occurs. The rate of oxidation will be related to the number of active species reaching the pore wall. This will be dependent on the number of species produced, and hence the open pore volume of the graphite. Furthermore the rate will be affected by the fraction of these species reaching the graphite surface; this will depend upon the mean distance active species must travel to reach the walls of the pore and hence upon the pore dimensions.

In a situation where the fraction of the active species reaching the pore wall is almost the same throughout the porosity, as will be the case in pure CO₂, or CO₂ containing only very small amounts of CO, the rate of oxidation should be proportional to the open pore volume.

Standring and Ashton (1965) quote oxidation rates at low weight loss for a number of graphites in CO₂ as a function of initial open pore volume. Fig A1.2 shows these rates normalised to that for PGA graphite, the material used to fabricate the cores of UK Magnox power stations; the relationship is clearly linear.

Taking this as a starting point, and assuming that radiolytic oxidation occurs uniformly throughout the porous structure, the initial rate of radiolytic oxidation can be expressed as

$$R_0 = k\varepsilon_0 G \quad (\text{A1.2})$$

where R_0 is the initial oxidation rate per unit dose, k a constant, and ε_0 the initial open pore volume. G is the effective G-value for production of oxidising species, that is the true G-value modified to allow for the fraction of species reaching the surface. To extend this expression to cover situations where the porous structure of the graphite has been modified by oxidation, it is necessary to account for two effects: the enlargement of open porosity by the oxidation process, and the accessing of initially closed porosity by oxidation. It is straightforward to determine the increase in open pore volume from the crystal density of graphite and the weight loss. Standring and Ashton investigated the change in closed porosity associated with oxidation; their data are consistent with a model where about 40% of the initially closed porosity is opened up at very low weight losses and the remainder hardly at all, at least up to weight losses of 30%. This leads to a model for the evolution of porosity which can be expressed as

$$\varepsilon = \varepsilon_e + \alpha W \quad (\text{A1.3})$$

In this expression ε is the instantaneous open pore volume, α a constant and W the weight loss. The initial opening of closed porosity is accounted for by using an effective value for initial open pore volume, ε_e , rather than the true value, ε_0 .

Using these two expressions, Standring (1966) demonstrates that the weight loss, W , at any dose, D , is given by

$$W = \frac{\varepsilon_e}{\alpha} \left[\exp \left| \frac{\alpha R_0 D}{\varepsilon_e} \right| - 1 \right] \quad (\text{A1.4})$$

Whilst this expression is effective for calculating weight loss as a function of dose at modest weight losses in the presence of small concentrations of relatively weak gas-phase inhibitors like CO, it suffers from the manifest shortcomings that the weight loss is not constrained to a maximum value of 100%, and that the rate of oxidation will increase indefinitely with weight loss. These difficulties are the result of the implicit assumption that the effective G-value does not vary with weight loss. In reality this cannot be so, as the increase in pore size will result in a smaller fraction of the active species reaching the surface of the graphite and hence a decreasing G-value. In the presence of more effective gas-phase inhibition this effect becomes important at weight losses of technological significance.

Graphite inhibition allowing for pore growth and surface inhibition

In an attempt to overcome the deficiencies described above, and also to account for the presence of surface inhibition by methane, the following empirical expressions, quoted by *inter alia* Kelly (1985) and based loosely on the Standring equation, have been widely used to calculate the rate of graphite oxidation in CO₂/CO/CH₄ gas mixtures:

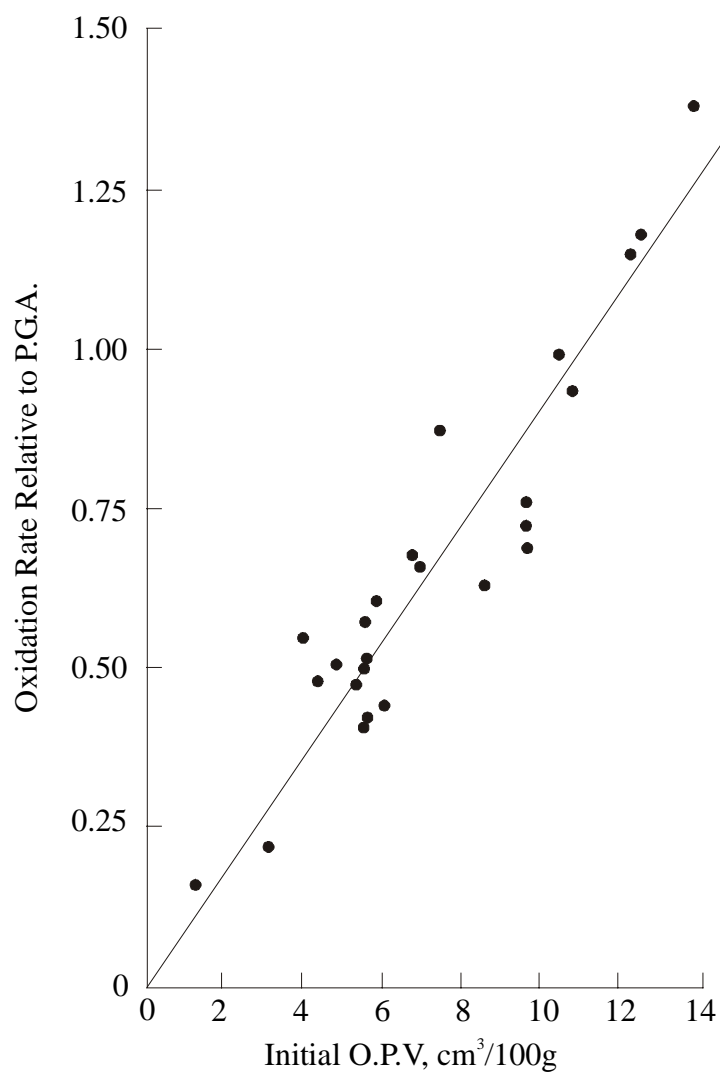


Figure A1.2 Oxidation rate of graphites relative to PGA as a function of open pore volume

$$W = d_1 \left| \frac{dx}{dD} \right|_0 \left[\exp\left(\frac{D}{d_1}\right) - 1 \right] \quad \text{for } D \leq 1.1d_1 \quad (\text{A1.5})$$

$$W = d_1 \left(\frac{dx}{dD} \right)_0 \left[3 \left(\frac{D}{d_1} \right) - 1.296 \right] \quad \text{for } D \geq 1.1d_1$$

where $(dx/dD)_0$ is the initial rate of graphite oxidation for the gas composition of interest, interpolated from the curves in Fig A1.3, and d_1 is a constant. The agreement of these equations with weight loss data obtained in MTR experiments is shown in Fig A1.4. It should be noted that the gas composition used to determine $(dx/dD)_0$ is not that in the bulk gas but that in the graphite porosity. This will differ from that in the bulk, as CO is generated by the oxidation process and methane destroyed by radiolysis.

As described above there are two possible mechanisms for surface inhibition: blocking access to active sites, or the formation of a sacrificial layer. The second of these two mechanisms has been modelled in some detail by Johnson (1981). If the number of oxidising species reaching the wall of a pore in unit time is J_{ox} then

$$J_{ox} = \xi \left| \frac{x}{L} \right| N_p \quad (\text{A1.6})$$

where N_p is the number of species produced in the pore in unit time, and $\xi(x/L)$ the probability that an oxidising species with mean diffusion length L will reach the wall of a pore with characteristic dimension x . The flux of depositing species, J_d , is given by

$$J_d = \left\{ 1 - \xi \left| \frac{x}{L} \right| N_p \left\{ \frac{k_2[CH_4]}{k_1[CO] + k_2[CH_4]} \right\} \right\} \quad (\text{A1.7})$$

where the term in the last set of braces represents f , the fraction of active species in the gas-phase deactivated by collision with methane. It is therefore straightforward to show that the net flux of oxidising species, J , is given by

$$J = N_p \left\{ \xi \left(\frac{x}{L} \right) - \left[1 - \xi \left(\frac{x}{L} \right) \right] f \right\} \quad (\text{A1.8})$$

It is clear from the model that, given that the value of the function $\xi(x/L)$ decreases with increasing x , there exists a pore with characteristic dimension x_t where the flux of oxidising species equals that of depositing species; that is

$$\xi \left| \frac{x_t}{L} \right| \{1 + f\} = f \quad (\text{A1.9})$$

Pores larger than x_t are net depositing and will shrink, pores smaller than this are net oxidising and will grow. In principle therefore, given the pore size distribution for the graphite, it is possible to calculate the weight loss by integrating the oxidising flux over the pores in the

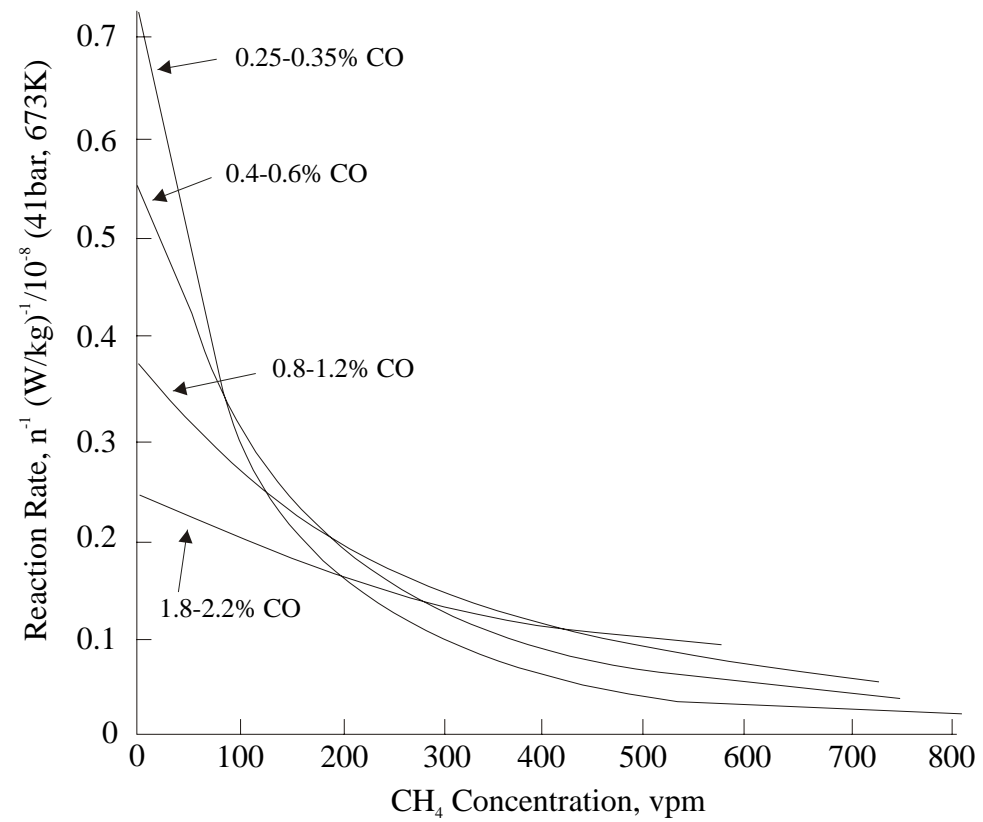


Figure A1.3 Initial oxidation rates of moderator graphite in coolant gases of different composition

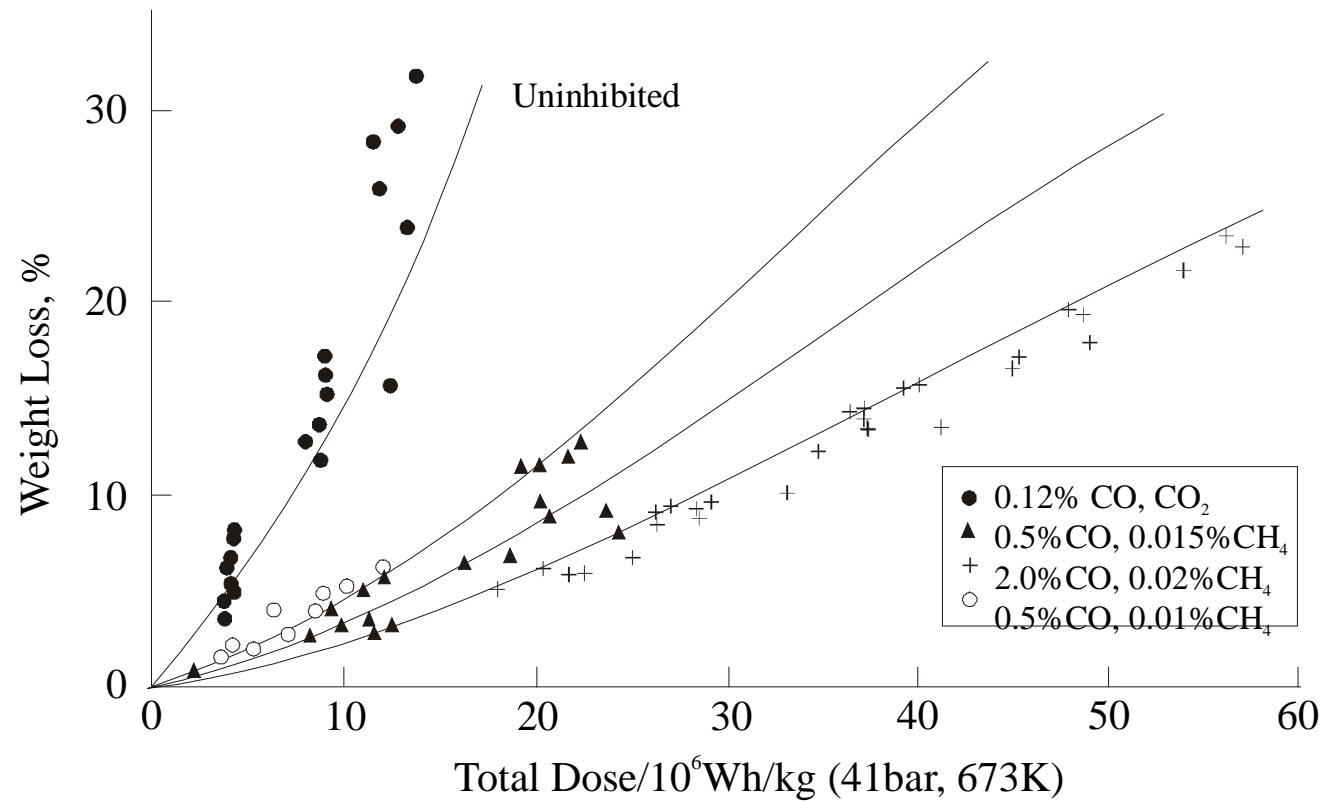


Figure A1.4 Moderator weight loss against dose in different coolants

size range $x = 0$ to x_i . In practice there are a number of difficulties with this approach, not least of which is defining the shape of the pores, upon which the form of the function $\xi(x/L)$ depends. The theory has, however, been worked rigorously for pores in the form of cylinders, spheres and infinite slabs. This gives the following expressions, where the characteristic dimension x is the half-width of a slab pore, and the radius of a cylindrical or spherical pore, and I_0 and I_1 are zero and first order Bessel functions:

$$\begin{aligned}
 \text{Slab - shaped pore:} \quad \xi\left(\frac{x}{L}\right) &= \frac{L}{x} \tanh\left(\frac{x}{L}\right) \\
 \text{Cylindrical pore:} \quad \xi\left(\frac{x}{L}\right) &= \frac{2L}{x} \frac{I_1(x/L)}{I_0(x/L)} \\
 \text{Spherical pore:} \quad \xi\left(\frac{x}{L}\right) &= \frac{3L}{x} \left[\coth\left(\frac{x}{L}\right) - \frac{L}{x} \right]
 \end{aligned} \tag{A1.10}$$

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