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A SURVEY OF
THE STORAGE BEHAVIOUR OF URANIUM DIOXIDE

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ABSTRACT

        The storage behaviour of uranium dioxide powder is reviewed. Topics
covered include the amount of oxygen taken up under storage conditions, the
basic oxidation processes, the effects of extra oxygen on the fabrication and
irradiation behaviour of uranium dioxide, the pyrophoric reaction of uranium
dioxide powders in air, the stabilization of uranium dioxide against oxidation,
and the effectiveness of sealed containers. The pyrophoric process in air at
room temperature is shown to be the result of rapid chemisorption of oxygen,
and a theory explaining this effect is developed. Equations are also derived
to describe the overall oxidation behaviour in air at room temperature, and
they are found to agree with what few experimental data are available.

CONTENTS

1. INTRODUCTION

In air at room temperature, the most stable uranium oxide is UO_3[1]. Thus UO_2 shows a strong tendency to take up oxygen on exposure to the air. The rate and practical extent of oxidation are functions of the temperature, the partial pressure of oxygen and the physical properties of the dioxide specimen[2]. The presence of oxygen in excess of the stoichiometric ratio of 2 may affect the fabrication behaviour of a UO_2 powder, and if excess oxygen is retained in the sintered product, the performance of the material under neutron irradiation may also be affected. Under some conditions, UO_2 powders may even burn in contact with air[2], an event which is obviously undesirable. Thus the behaviour of UO_2 powders under storage conditions should be of concern to anyone involved in the production or handling of these materials. In this review both practical and theoretical aspects of this topic are considered.

2. STORAGE - GENERAL RESULTS

The primary reaction which can occur during the storage of UO_2 is oxidation[2], involving both chemisorption and penetration of the oxygen into sub-surface regions. There is no evidence that the adsorption of other gases, for example CO_2 and water vapour, is a major problem. This is not to say that these other gases are not adsorbed or that they are without effect on the subsequent behaviour of UO_2, and there appears to be scope for research in this area. However, oxidation during storage is the topic covered in the remainder of this survey.

The oxidation of UO_2 with free access of air above room temperature was studied by Stevenson and Boyd[3] and the results were summarised by Martin[4]. The process had an activation energy of 13 to 17 kcal/mole and this was used to make predictions about the oxidation rate in the vicinity of room temperature. The rate of oxidation for two samples of slightly differing specific surface was approximately proportional to the specific surface, and other workers [5,6,7] have observed that the O/U ratio attained after extended storage is directly related to the specific surface. The predictions were expressed in terms of the percentage of U_3O_8 formed. Some of the quoted results have now been recalculated as O/U ratios and are given in Table 1, together with values calculated for other specific surfaces assuming that the oxidation rate is directly proportional to the specific surface.

More recent work on the oxidation of UO_2 (see Section 3) indicates that these results may not be completely reliable. The temperature range of experimentation was such that at least three different oxidation processes were probably active,

so that there was probably no justification for extrapolating to room temperature by assuming a unique mechanism.

Table 2 gives results of other experimenters[6,7] for the variation in the limiting O/U ratio with specific surface after storage in air. The values due to Lister and Gillies[6] were taken from a graph in their paper, whereas those of Bell and Carteret[7] are as quoted in their work. In neither case were the actual experimental conditions reported.

The two sets of results disagree, those of Lister and Gillies[6] indicating a much higher degree of oxidation. Their results also agree better with the two-year values given in Table 1. The question of the limiting O/U ratio is discussed again in Section 7, and it is sufficient to point out here that there are no thoroughly reliable data for the oxidation behaviour of UO_2 under storage conditions.

Humidity in the air has been thought to enhance the oxidation rate[2], but controlled experiments[4,8] have shown it to have no effect.

The oxidation of UO_2 during storage may be limited by using tightly sealed containers[4], and optimum conditions are stated to involve airtight containers held at 25°C or less[2].

3. OXIDATION

There appear to be three or even four distinct stages in the oxidation of UO_2. In the present survey we are concerned with three stages, which may be identified in the following way.

Stage 1. Chemisorption. This occurs rapidly on a clean, reduced surface at all temperatures, even as low as -183°C[9]. The chemisorption limit appears to correspond to one oxygen atom for each surface uranium ion[9]. The heat of chemisorption at -183°C decreases from about 55 kcal/mole at zero coverage to 10 to 12 kcal/mole at half coverage, and then to ~ 5 kcal/mole at the chemisorption limit[10]. As the adsorbed oxygen approaches the chemisorption limit there is evidence that impinging oxygen is at first physically adsorbed, then slowly changes to the chemisorbed state[10].

Stage 2. Sub-surface oxidation. This process becomes noticeable at about -138°C and up to about 50°C is the major process responsible for additional oxidation[11,12]. At constant temperature the amount of oxygen taken up (in addition to that chemisorbed) follows a law of the form:

$$dy/dt = K \exp(-ay) \qquad \ldots\ldots(1)$$

where y is the extra oxygen adsorbed, the constant K depends on temperature and pressure, and a appears to depend only on temperature[11,12]. For materials of similar preparation, the oxidation rate is directly proportional to the specific surface[11,12]. The oxidation rate increases with temperature, the apparent activation energy increasing from about 6 kcal/mole at the lower temperatures to about 15 kcal/mole above 0°C[11]. The maximum additional oxygen taken up in this stage is stated to be about four times that contained in the chemisorbed layer[11,12]. It is believed to penetrate into the sub-surface regions of the UO_2, the estimated penetration distance being about 40Å if one extra oxygen atom is taken up per unit cell and 10Å if the oxidized layer has a composition of UO_3[11]. Hoekstra, Santoro and Siegel[13] have observed infrared absorption peaks characteristic of UO_3 in high surface area UO_2 oxidized at room temperature.

Stage 3. Bulk oxidation. A new process of oxidation becomes dominant at about 80 to 100°C[12,14,15]. For material of > $2m^2$/g specific surface the oxidation obeys a diffusion law with an activation energy of 20 to 27 kcal/mole, and continues up to an O/U ratio of 2.33[15]. The reaction probably involves the formation of a layer of composition U_3O_7 which thickens as oxidation proceeds[14]. Further oxidation to U_3O_8 generally requires a temperature of about 200°C[14]. For material of very low surface area the oxidation process is apparently one of nucleation and growth[15].

4. FABRICATION OF UO_2 - THE EFFECTS OF STORAGE

Of the various techniques[2] which may be used to fabricate nuclear fuel elements from UO_2 powders the one using cold pressing and sintering is the most common and the only one to be considered here. Storage may influence this process by affecting either the pressing or the sintering behaviour of the powder.

Although one suspects that surface oxidation and storage should affect pressing behaviour, which is related to the surface properties of the powder, there is little in the literature to support this belief. This lack of data presumably results from the widespread use of pressing aids with UO_2, so that the pressing characteristics are determined largely by the particular binder and/or lubricant used. Thus if pressing aids are to be used, storage will probably not unduly affect the pressing behaviour of UO_2. It is assumed of course that oxidation during storage has been non-pyrophoric, and the powder has not been completely converted to U_3O_8 or UO_3. In the absence of pressing aids, the pressing behaviour might well be sensitive to storage, and the region of maximum effect would probably correspond to the establishment of a chemisorbed monolayer of oxygen.

The presence of oxygen in excess of the stoichiometric ratio has a marked effect on the sintering rate of UO_2[2]. Excess oxygen increases the sintering rate and decreases the activation energy for sintering[16]. The major effect occurs within the range $2.00 \leq O/U \leq 2.04$[17]. Thus an improvement in sintering rate or a reduction in the required sintering temperature may be achieved by increasing the O/U ratio, either by air-oxidation[18] or by incorporating a powder with higher oxygen content[19]. Variations of these two processes have been patented[20-24]. In general the super-stoichiometric materials are sintered in a 'neutral' atmosphere such as nitrogen or argon. They may also be sintered in a reducing atmosphere such as hydrogen or cracked ammonia, in which case the excess oxygen may[25] or may not[5] give increased sintering rates. Presumably this depends on its rate of removal in the reducing environment[26].

Thus the major effect of storage would appear to be an enhancement of the sintering rate of the UO_2 powder, if it is sintered under neutral or mildly reducing conditions. The effect is most pronounced for the initial departure from stoichiometry and is less sensitive to additional oxygen taken up by already well-oxidised powders. Where storage leads to variations in oxidation either within or between otherwise identical batches of powder, there may be corresponding variations in sintering rate unless a strongly-reducing atmosphere is used during the sintering.

5. IRRADIATION PERFORMANCE OF UO_2 - THE EFFECTS OF STORAGE

The effects of excess oxygen on the irradiation behaviour of sintered UO_2 have been summarized well by Robertson[27]. In general, excess oxygen is a disadvantage. Relative to stoichiometric UO_2 the thermal conductivity is reduced, the thermal expansion is increased, the diametral expansion under irradiation is increased and the fission product release rate is increased[27]. The latter property is the most sensitive to typical amounts of excess oxygen in sintered UO_2 and will normally determine the allowable O/U ratio. The plasticity and volatility of UO_2 are also enhanced by excess oxygen[27]. The allowable O/U ratio in UO_2 fuel elements depends on the reactor design, and for the CANDU reactor the value is ≤ 2.01[27]. Thus in general it is preferable that the fabricated oxide be close to stoichiometric.

6. PYROPHORICITY

6.1 General

Whether or not a given UO_2 preparation will spontaneously ignite when exposed to oxygen depends on the specific surface of the oxide, the condition of the surface, the partial pressure or availability of oxygen and the temperature[2].

Anderson et al.[28] report that fully-reduced powders of specific surface 8.4 to 12.9 m^2/g were pyrophoric in air at room temperature, whereas ones with specific surface < 2 m^2/g were not pyrophoric. A specimen of specific surface 10.3 m^2/g was pyrophoric in oxygen at 0°C, but non-pyrophoric if pre-oxidized at -80°C[12]. Further examples of pyrophoricity protection by pre-oxidation or adsorption of other vapours are listed in Section 7. Specimens of specific surface 1.4 m^2/g were non-pyrophoric up to 50°C but pyrophoric at 150°C[12].

6.2 Theory

The general conditions which determine whether a given powder is pyrophoric when exposed to air at room temperature may be identified in the following way. Consider an isolated particle undergoing oxidation. Its temperature will rise when the rate of heat generation caused by oxidation exceeds the rate of heat loss from the particle. This condition may be expressed by the heat balance:

Rate of heat generation - Rate of heat loss = Rate of increase in heat content
$$\ldots\ldots(2)$$

The rate of heat generation per particle is directly proportional to the number of moles of oxygen reacting with unit surface area per second, $(dx/dt)_{x,T,p}$, the heat of reaction per mole, $\Delta H_{x,T}$ and the surface area of the particle, S. The rate of heat loss per particle is directly proportional to the difference between the particle temperature T and the environment temperature T_e, and to the surface area S and the heat transfer coefficient h, whilst the rate of increase in heat content of the particle is the product of the particle mass m, its specific heat c and the rate of temperature rise (dT/dt).

Thus Equation 2 becomes:

$$\Delta H_{x,T} \, S \, (dx/dt)_{x,T,p} - h \, S \, (T-T_e) = m \, c \, (dT/dt) \qquad \ldots\ldots(3)$$

The subscripts x, T and p indicate that in general ΔH and (dx/dt) are functions of the specified variables.

Let the particle be spherical, with diameter D. Thus $S = \pi D^2$ and $m = \pi D^3 \rho/6$ where ρ is the particle density. Substitution in Equation 3 gives:

$$\Delta H_{x,T} \, (dx/dt)_{x,T,p} - h \, (T-T_e) = (c\rho D/6) \, (dT/dt) \qquad . \; \ldots\ldots(4)$$

In principle, if (dx/dt) and ΔH were known as functions of x and T, for a given pressure, and if h and T_e were also known, the entire temperature - composition - time history of the particle could be calculated and any pyrophoric tendency identified. All the required data are not available, but Equation 4 at least

indicates the determining variables. We see that:

(i) For a given x, T, T_e and p, (dT/dt) is proportional to (1/D). Thus the pyrophoric tendency increases with decrease in particle size or increase in specific surface.

(ii) For a given T, T_e, p and D, (dx/dt) for Stages 2 and 3 and Δ H for Stage 1 decrease sharply with increase in $x^{(10,12)}$. Thus the pyrophoric tendency decreases with increase in prior oxidation.

(iii) For a given x, T_e, p and D, (dx/dt) increases rapidly with increase in temperature for Stages 2 and 3 oxidation[2,12]. Thus the pyrophoric tendency increases markedly with increase in particle temperature.

(iv) For a given x, T, T_e and D, (dx/dt) decreases with decrease in the oxygen partial pressure below atmospheric in Stages 2[12] and 3[3] and probably also Stage 1 oxidation. Thus the pyrophoric tendency decreases with decrease in oxygen pressure. A further effect of very low oxygen pressures would be to limit the amount of available oxygen.

(v) For a given x, T, p and D, the pyrophoric tendency will obviously increase with increase in T_e and with decrease in h.

Some quantitative idea of the pyrophoric process at room temperature may be gained by substituting data for the chemisorption reaction in Equation 4. The hypothesis is that a pyrophoric reaction occurs at room temperature when the heat liberated in the chemisorption stage is sufficient to heat the particle to a temperature where Stages 2 and 3 oxidation are rapid enough to ensure a continued increase in temperature. That pyrophoricity at room temperature depends on the chemisorption reaction is justified by the fact that at room temperature[12] Stage 2 oxidation is quite slow and Stage 3 almost non-existent whereas chemisorption is virtually instantaneous. An estimate of the time required to produce a mono-layer of oxygen when the substance is exposed to room-temperature air gives 10^{-8} seconds for a condensation coefficient of unity and 10^{-3} seconds if the condensation coefficient is as low as 10^{-5}. Pyrophoricity is evident immediately on exposure to air, there being no incubation period before ignition. Because of the fast chemisorption rate we may ignore the heat loss term in Equation 4 and substitute:

$$(dx/dt)_{x,T,p} \sim n/N \ \Delta t$$

$$\Delta H_{x,T} \sim 3 \times 10^4 \text{ cal/mole}^{(10)} \text{ (an average value)}$$

$$c = 0.055 \text{ cal/g } (°C)^{(14)}$$

$$\rho = 11 \text{ g/cm}^3$$

and (dT/dt) = $\Delta T/\Delta t$,

where n is the number of molecules of oxygen in the chemisorbed layer, N is Avogadro's Number, Δt is the time needed to establish the monolayer, and ΔT is the temperature rise of the particle. The value of n is approximately 4 x 10^{14} molecules/cm² (Section 7). The calculations give:

$$\Delta T \sim 2 \times 10^{-4} /D \qquad\qquad .....(5)$$

Calculated values of ΔT for various values of specific surface and particle diameter D are given in Table 3, and appear to substantiate the present approach.

Powders which are known to be pyrophoric at room temperature (specific surface $\geq$ 8.4 m²/g) have values of ΔT which would boost their temperatures to the point where Stage 2 oxidation is extremely rapid and Stage 3 oxidation is just beginning, whereas non-pyrophoric powders (< 2 m²/g) involve much smaller temperature rises. A further point of course is that the required temperature rise would be smaller for fine powders than for coarse ones, since the rates of Stages 2 and 3 oxidation depend directly on specific surface.

7. STABILIZATION

The term stabilization applied to UO_2 powders appears to have four possible meanings:

(i) complete protection of the powder against any oxidation,

(ii) protection against a pyrophoric reaction with air,

(iii) limiting the rate of air-oxidation to an acceptable level, and

(iv) limiting the extent of air oxidation.

In the commercial production of a sinterable UO_2 powder it is considered neither feasible nor necessary to ensure complete protection against oxidation, and, in general, stabilization probably involves a combination of the other three meanings. There are three basic techniques which may be used.

7.1 Surface Area Control

The rate of oxidation of a powder increases with increase in surface area per gram[2]. Thus a powder may be 'stabilized' by reducing its specific surface (for example, by heating to an appropriate temperature in hydrogen). This philosophy tends to run counter to the requirement of a high specific surface for

good sinterability. However, it is still logical to ensure that the specific surface of the as-produced powder is no greater than that required for the desired sinterability.

7.2 Oxidation

Since the total heat generated in the chemisorption stage increases with oxygen take-up during chemisorption, the pyrophoric reaction may be prevented by prior oxidation. Chemisorption of oxygen at low temperatures or under conditions of limited oxygen access would thus prevent room-temperature pyrophoricity in a potentially pyrophoric powder. The amount required to form one chemisorbed layer on a freshly reduced UO_2 surface may be estimated as 4×10^{14} molecules of oxygen per square centimetre of surface, using the results of Roberts[9,11]. This gives the following relationship between the O/U ratio and the specific surface S of the powder for a complete layer, and thus protection against room temperature pyrophoricity:

$$O/U = 2.000 + 3.6 \times 10^{-3} S, \quad \text{where S is in } m^2/g. \quad .....(6)$$

Thus a powder with specific surface 10 m^2/g would require surface oxidation to O/U ~ 2.04 to be sure of preventing a pyrophoric reaction in air, and a powder with specific surface 100 m^2/g would require surface oxidation to O/U ~ 2.36. In practice, particularly with the medium surface area powders, less than a complete layer (and thus a somewhat lower O/U ratio) would probably be sufficient. Re-oxidation techniques include oxidation by water vapour at the previous reduction temperature[29,30] or by a dilute oxygen-nitrogen mixture at room temperature[31].

Prior oxidation in excess of the chemisorption limit will decrease the rate of oxidation in Stages 2 and 3. The extent of this effect may be calculated by deriving the overall oxidation law, containing contribution from Stages 1, 2 and 3, for a freshly reduced UO_2 powder exposed to air at room temperature. If Δ (O/U) is the excess in O/U ratio above 2.00, the contributions of the various stages are given by:

Stage 1: $\quad \Delta (O/U)_1 = 3.6 \times 10^{-3} S \quad .....(7)$

Stage 2: $\quad \Delta (O/U)_2 = S \log_e(1.03t)/1400 \quad .....(8)$

Stage 3: $\quad 1 - [1-3\Delta(O/U)_3]^{1/3} = 3.68 \times 10^{-6} St^{\frac{1}{2}} \quad .....(9)$

Equation 7 comes directly from Equation 6. Equation 8 was derived from the observed rate law for Stage 2 (Equation 1), using $\underline{a} = 9$[12] and K = 0.115 at 25°C and atmospheric pressure. K was calculated from the observation that a carefully

pre-oxidized specimen with specific surface 10.3 m^2/g reached an O/U ratio of 2.18 after 2 weeks in air at room temperature[12]. Under these conditions the contributions of Stages 1 and 3 were first calculated using Equations 7 and 9, and subtracted from the total increase in O/U ratio to give the contribution from Stage 2. Equation 9 was obtained from the rate data of Blackburn et al.[2,32] and refers to a temperature of 25°C.

$$\text{Taking } \Delta (O/U) = \Delta (O/U)_1 + \Delta (O/U)_2 + \Delta (O/U)_3 \quad .....(10)$$

we obtain:

$$O/U = 2.000 + 3.6 \times 10^{-3} S + S \log_e(1.03t)/1400 + [1-(1-3.68 \times 10^{-6} St^{\frac{1}{2}})^3]/3 . \quad .....(11)$$

In Equations 7, 8, 9 and 11 the units of S are m^2/g and those of t are seconds. Equation 11 may be used to calculate O/U ratios for various values of S and t, and results are given in Table 4.

The O/U ratio as a function of time has also been calculated for material of specific surface 0.455 m^2/g, for direct comparison with values taken from Table 1. The two sets of results are plotted against time in Figure 1, and they agree very well. Thus the data in Table 1 may be quite reliable, in spite of the treatment as one unique process of a phenomenon composed of three quite different oxidation processes.

The results given in Table 4 are plotted in Figure 2. The O/U ratio in excess of 2.00 is almost directly proportional to specific surface for a given exposure time (Equation 11), and the relationships for various times are plotted in Figure 3. The predictions agree well with the observations of Lister and Gillies[6] (Table 2) but not with the data of Bel and Carteret[7] (Table 2), and it is suggested that the latter values reflect either insufficient exposure times, materials stabilized by other means, or storage with limited access of air.

Figures 2 and 3 may be used to estimate the oxidation rate for a powder of a given specific surface and O/U ratio. For example a powder of specific surface 5 m^2/g and O/U ratio 2.18 should gain a further 0.032 in O/U ratio after 1 year in air and an additional 0.024 in a subsequent year. For a particular specific surface, Figure 2 can yield the O/U ratio to produce a desired oxidation rate as well as the time needed to establish that O/U ratio on exposure to air at room temperature. Thus Figure 2 is useful where stabilization is defined in terms of an acceptable rate of oxidation. It is also useful where stabilization is defined in terms of a limiting O/U ratio, since it indicates whether that ratio would be

exceeded for the expected storage time with free access of air. This in turn would indicate whether the air access to the powder must be restricted or some other measure taken to reduce the oxidation rate.

7.3 Adsorbed Inhibitors

All stages of oxidation at room temperature may be retarded or perhaps even prevented by adsorbing some other species on the UO_2 surface. Suitable materials include water vapour[33,34,35], carbon dioxide[33,34,36], ammonia[34,35], carbon tetrachloride[34,35], or various alcohols, ketones or hydrocarbons[34,35]. Carbon dioxide does not completely prevent subsequent oxidation, but does prevent a pyrophoric reaction with air[36]. These gaseous inhibitors are usually adsorbed at room temperature[35,36], and there is no report of any subsequent effect on the fabrication behaviour of the oxide powder.

8. LIMITING THE ACCESS OF AIR

Storage in tightly sealed containers[4] might be expected to reduce both the rate and the extent of oxidation of UO_2. In order to estimate the likely effectiveness of this procedure, calculations were performed for the following storage conditions:

Mass of UO_2 =   10 kg

Volume of container   =   10 litres

Thickness of container wall $\dot{=}$ 2 mm.

It was assumed that all the oxygen penetrating the container reacted immediately with the UO_2, so that the oxygen partial pressure drop across the container wall was equal to the atmospheric partial pressure of oxygen. The permeability coefficient K required for a particular oxidation rate was calculated using the formula[37]:

$$K = Q_1 P_1 \ell / At \Delta p \quad , \qquad \qquad \dots\dots(12)$$

where Q_1/t is the flow rate of oxygen at S.T.P., p_1 is the external oxygen partial pressure, ℓ is the container wall thickness, A is the container surface area and Δp is the oxygen partial pressure drop across the container wall.

An oxidation rate of 0.01 per year change in the O/U ratio was calculated to require a permeability coefficient of $< 10^{-7}$ cm^2/sec, and a rate of 0.1 per year would require $K < 10^{-6}$ cm^2/sec. Values below 10^{-7} cm^2/sec should be readily attainable for the container material. For example, steel, glass and probably polythene containers should be suitable, but fibre drums would be too permeable.

The degree to which the containers must be sealed may be illustrated by calculating the size of a single hole which, by itself, would give the desired maximum oxidation rate. The assumption is that oxygen enters the container by diffusion through the oxygen-nitrogen mixture contained in a cylindrical hole of radius r and length 2 mm. The relevant form of the Fick equation[37], together with the data for the diffusion coefficient of oxygen in air[38], indicates that when the container material has a negligible permeability, a cylindrical hole of 0.1 mm dia. would produce an oxidation rate no greater than 0.01 change in the O/U ratio per year. Sealing to this degree should be possible in industrial practice.

It is probably not necessary to remove the air from the container before filling it with UO_2. For the above reference conditions, the oxygen in the container at atmospheric pressure would be sufficient to increase the O/U ratio by only 0.004.

9. DISCUSSION AND CONCLUSIONS

The major points in the previous sections may be summarized as follows:

Freshly-reduced uranium dioxide oxidizes readily on exposure to air at room temperature. The oxidation rate is proportional to the specific surface of the powder. The oxidation reaction includes strong and very rapid chemisorption, a subsequent stage involving limited penetration of the UO_2 lattice, and a third stage with diffusion kinetics. The third stage becomes of significant importance for exposure times greater than a few months and at one year it is expected to be the major process. The chemisorption process is strongly exothermic and for material of high enough specific surface the heat generated is sufficient to start a pyrophoric reaction. A freshly reduced powder of specific surface 8 m^2/g is expected to be pyrophoric in air. The transition point between pyrophoric and non-pyrophoric powders in air at room temperature lies between 2 and 8 m^2/g and is probably closer to 8 m^2/g. Experiments are required to establish the transition point. Room temperature pyrophoricity may be prevented by minimizing the amount of oxygen chemisorbed or the chemisorption energy, and suitable techniques include limiting the availability of oxygen, prior oxidation at either low temperatures or with limited access of oxygen, and the use of gaseous inhibitors such as water vapour or CO_2.

The extent of oxidation in air increases with time and specific surface of the powder and for reasonably high specific surfaces considerable oxidation may occur over normal storage periods. There is disagreement in the literature over the O/U ratios to be expected and the theoretical analysis in this review supports the more pessimistic values. Tables and graphs presented here enable the oxidation tendency to be predicted and a decision made as to whether some degree of protection

is required. Protective methods include the use of air-tight containers and adsorbed gaseous inhibitors. Air-tight containers must be relatively impervious if they are to be effective for prolonged storage periods. Adsorbed gaseous inhibitors appear to be useful for oxidation protection, and an attractive one is water vapour. However, experiments would be needed to establish the optimum adsorption technique and the subsequent storage and fabrication behaviour of such powders.

Extra oxygen enhances the sinterability of UO_2 if it is even partly retained during sintering. However, retained oxygen is detrimental to the irradiation performance of UO_2 fuel. The extra oxygen would tend to be removed during sintering in either neutral or reducing atmospheres, but if the residual level in the sintered piece is still too high then it may be lowered by subsequent reduction in hydrogen at or above the sintering temperature. The effect of oxygen on the sintering rate may lead to variations in sintering behaviour where there are differences in oxygen content either within or between batches of powder, unless the sintering conditions are such that the material is fully reduced before sintering begins.

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TABLE 1

CALCULATED O/U RATIOS AFTER STORAGE FOR VARIOUS TIMES IN AIR

Specific Surface (m²/g)	0.455[3,4]			1			5			10		
Temperature (°C)	10	20	30	10	20	30	10	20	30	10	20	30
Storage Time												
1 hour	2.0003	2.0003	2.0005	2.0006	2.0007	2.001	2.003	2.004	2.005	2.006	2.007	2.010
24 hours	2.002	2.004	2.006	2.005	2.009	2.014	2.026	2.044	2.070	2.051	2.088	2.14
7 days	2.006	2.007	2.008	2.013	2.016	2.018	2.066	2.077	2.092	2.13	2.15	2.18
30 days	2.007	2.009	2.011	2.016	2.019	2.024	2.081	2.096	2.12	2.16	2.19	2.24
60 days	2.008	2.010	2.012	2.018	2.021	2.026	2.088	2.11	2.13	2.18	2.21	2.27
6 months	2.010	2.012	2.015	2.021	2.026	2.034	2.11	2.13	2.17	2.21	2.27	2.34
1 year	2.011	2.013	2.018	2.024	2.029	2.039	2.12	2.15	2.20	2.24	2.29	2.39
2 years	2.012	2.016	2.021	2.026	2.035	2.046	2.13	2.18	2.23	2.27	2.35	2.46

TABLE 2

LIMITING O/U RATIOS AFTER STORAGE IN AIR

Specific Surface (m²/g)	0.61	0.78	1.1	1.4	1.8	2.7	5.5	10.9	Reference 6
O/U	2.01	2.02	2.03	2.04	2.06	2.13	2.27	2.43	
Specific Surface (m²/g)	1.2	3	7	10.5	11.5	12.5	17	19	Reference 7
O/U	2.00	2.06	2.13	2.21	2.22	2.21	2.25	2.29	

TABLE 3

CALCULATED TEMPERATURE RISES CAUSED BY CHEMISORPTION OF OXYGEN

Specific Surface (m²/g)	Particle Diameter (μ)	ΔT(°C)
0.1	5.5	0.4
0.2	2.7	0.7
0.5	1.1	2
1.0	0.55	4
2	0.27	7
5	0.11	18
10	0.055	36
20	0.027	74
50	0.011	180
100	0.0055	360

TABLE 4

PREDICTED O/U RATIOS DEVELOPED IN AIR AT 25°C

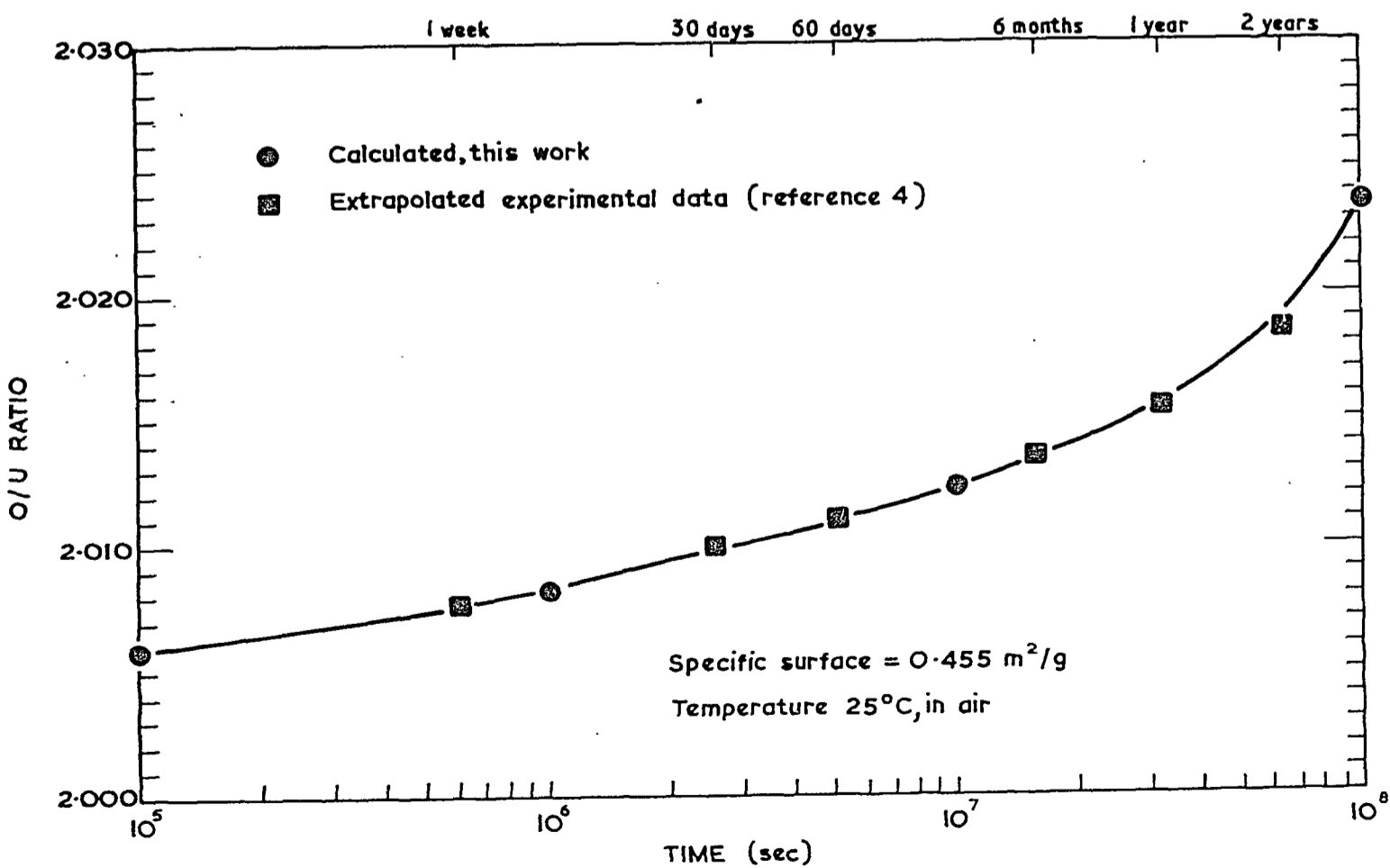| Time (sec)	Specific Surface (m²/g)									
	1	2	3	4	5	6	7	8	9	10
10^4	2.010	2.021	2.032	2.042	2.053	2.063	2.074	2.085	2.095	2.106
10^5	2.013	2.026	2.038	2.052	2.065	2.078	2.091	2.103	2.116	2.130
10^6	2.019	2.034	2.052	2.069	2.086	2.103	2.120	2.137	2.154	2.170
10^7	2.027	2.053	2.080	2.104	2.131	2.156	2.181	2.206	2.230	2.255
10^8	2.052	2.102	2.149	2.193	2.236	2.277	2.315	2.350	2.385	2.417

FIGURE 1. OXIDATION CURVE FOR UO_2 (SPECIFIC SURFACE 0.455 m²/g) EXPOSED TO AIR AT 25°C

P1184
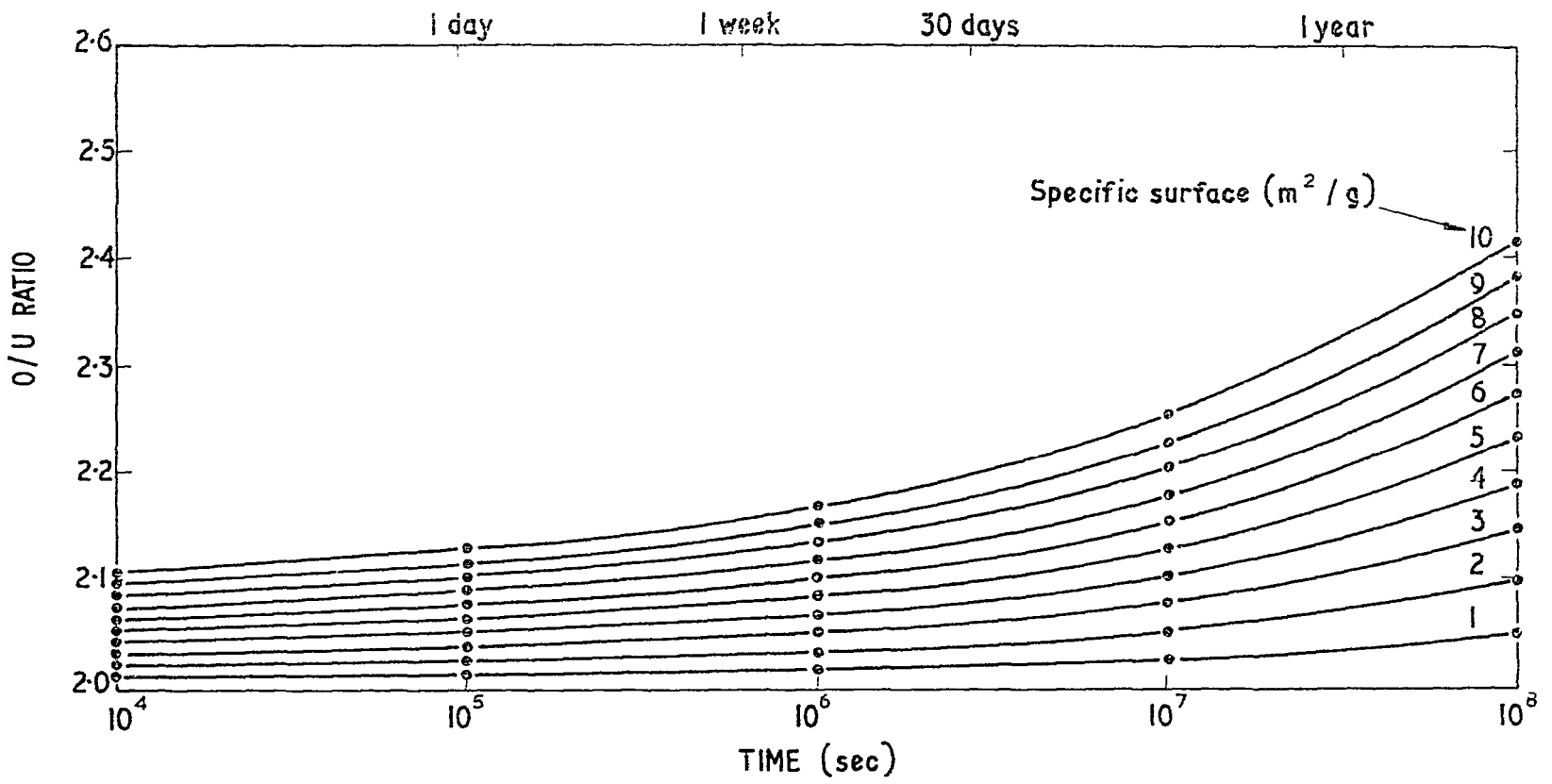
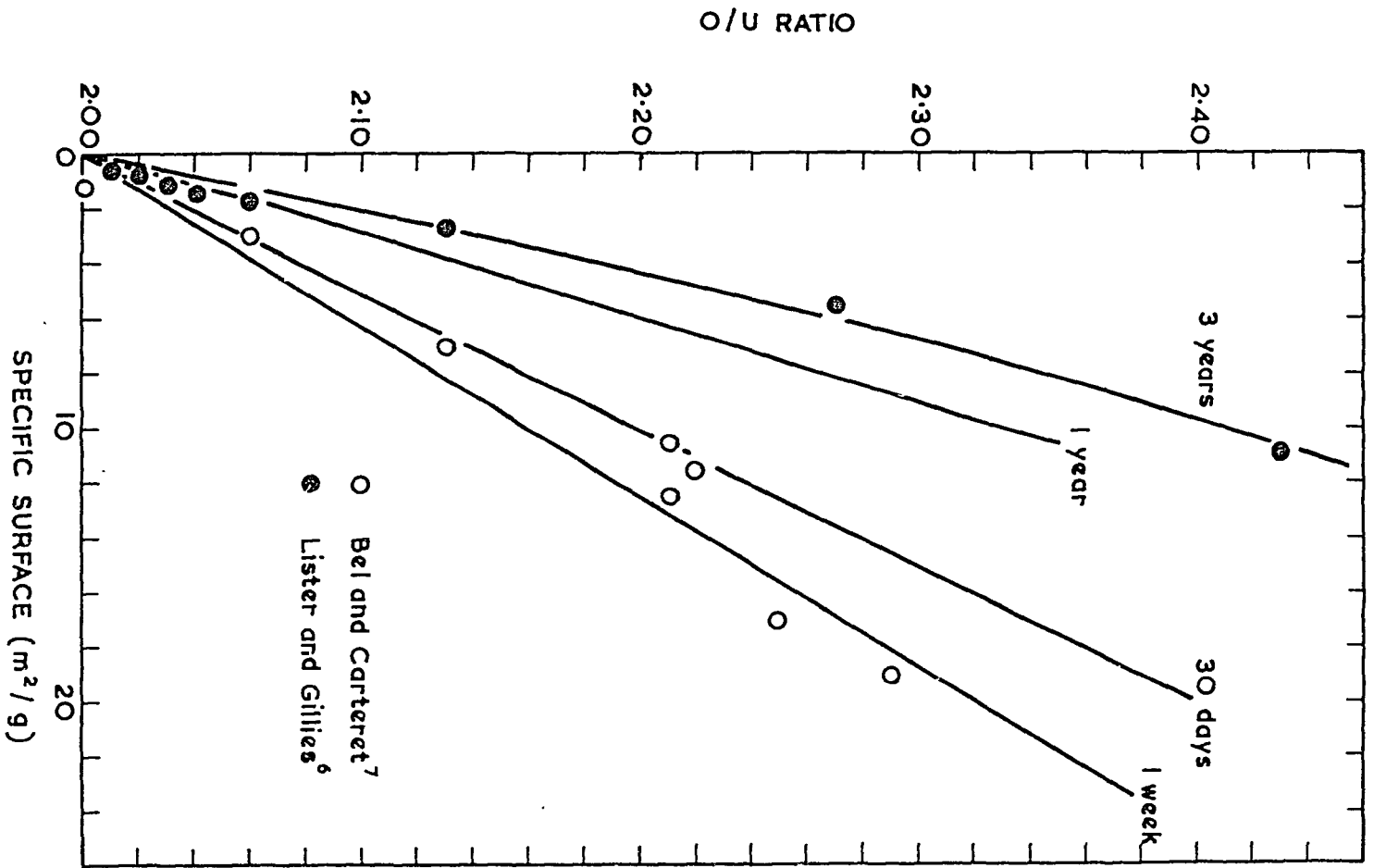FIGURE 2. OXIDATION CURVES FOR UO₂ (VARIOUS SPECIFIC SURFACES) EXPOSED TO AIR AT 25°C

P1184

FIGURE 3. RELATION BETWEEN O/U RATIO AND SPECIFIC SURFACE (EXPOSED TO AIR AT 25°C FOR VARIOUS TIMES)

P1184