

A study of the variables in the coating of fuel particles in a fluidised bed

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A STUDY OF THE VARIABLES IN THE COATING OF
FUEL PARTICLES IN A FLUIDISED BED

by

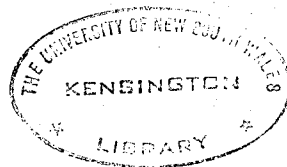
P.G. Alfredson

A Thesis Submitted to

THE UNIVERSITY OF NEW SOUTH WALES

for the Degree of

MASTER OF SCIENCE



Sydney, March 1964

I hereby certify that this work has not been submitted for the purpose of obtaining a higher degree from any other University or Institution.

Summaries of progress in this investigation have been reported jointly with Dr. R.C. Cairns in papers presented to the Symposium on Ceramic Matrix Fuels Containing Coated Particles, Battelle Memorial Institute, U.S.A., 5-6th November, 1962 (TID-7654, pp.411-420) and to the International Conference on Beryllium Oxide, Newport, Sydney, Australia, 21-25th October, 1963 (J. Nucl. Mat. - in press).

ABSTRACT

The coated fuel particle concept is a promising means of minimising fission product release from a fully ceramic dispersion fuel based on beryllium oxide for a high-temperature gas-cooled reactor system, if techniques can be developed to produce ceramic coatings of high integrity which are impervious to fission products.

Alumina and beryllia coatings have been successfully deposited on UO_2 and $(\text{U,Th})\text{O}_2$ particles by the hydrolysis of aluminium and beryllium chlorides with water vapour in a fluidised bed. The coated particles produced were evaluated by metallographic examination, Knoop hardness measurements, acid-leach and air-oxidation testing, measurement of alpha-particle emission, chemical analysis, heat treatment, and fission gas release measurements on post-irradiation annealing.

Coating properties have been shown to be a function of coating temperature, reactant feedrate ratio, and coating rate. For coating temperatures in the range 500 to 1100°C , best alumina coatings were deposited at 1000°C with an $\text{AlCl}_3/\text{H}_2\text{O}$ molar feedrate ratio of approximately 0.36 and a maximum coating rate of 2 to 3 microns per hour. At a coating temperature of 1000°C , best beryllia coatings were deposited using a $\text{BeCl}_2/\text{H}_2\text{O}$ molar feedrate ratio of about 0.5 and a maximum coating rate of approximately 3 microns per hour. Initial beryllia coating runs at a fluidised

bed temperature of 1400°C failed to produce uniform dense coatings. Evaluation results obtained for the alumina coatings were consistent with published data and confirmed the promise of alumina coated fuel particles for use in ceramic nuclear fuels, but further work is required to determine optimum conditions for the deposition of beryllia coatings.

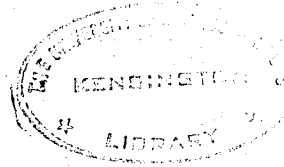
Possible mechanisms of coating deposition have been proposed. Coating buildup may occur as the result of a heterogeneous non-catalysed surface reaction, or a homogeneous gas-phase reaction followed by transport of the oxide product, or intermediate reaction products, to the surface of the particles where crystal growth occurs. The proportion of oxide deposited as coating on the particles depends on the solids-gas contact in the fluidised bed. Variations in coating properties with the conditions of deposition are explained in terms of changes in reaction equilibria, the formation of intermediate reaction products, and by classical nucleation and crystal growth theory.

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CHAPTER 1



INTRODUCTION

The Australian Atomic Energy Commission is making a study of a high-temperature gas-cooled reactor system moderated by beryllia in which the fissile and fertile material is dispersed as small particles throughout some or all of the moderator (1). Fuel cycles of interest use uranium-233, uranium-235 or commercial plutonium as the fissile element, and thorium-232 as the fertile element. The fuel particles should be at least 100 microns in diameter so that fission product damage is limited to the fuel particles and their immediate surroundings leaving the matrix substantially free from this damage (2).

To avoid certain limitations on the temperature of the outlet gas and thus be able to achieve steam cycles comparable with those in use in the most modern conventional power stations, the reactor core is to be completely ceramic without metallic canning to contain fission products. It is desirable for the coolant circuit to be free from fission products to eliminate the need for expensive fission product clean-up equipment, and permit practical maintenance of the primary circuit components. A fully ceramic dispersion fuel is required which will retain most, if not all, of the fission products.

The several possibilities for reducing fission product release to the coolant circuit include cladding the fuel elements with an impervious ceramic coating, and coating the individual fuel particles with an impervious ceramic layer before dispersion in the beryllia matrix. Coating of the particles eliminates the possibility of fuel material being exposed to the coolant gas and allows better fuel dispersion since particles are then separated by a distance at least equal to two coating thicknesses. Moreover with a coating which is denser than the matrix, the fission products may be retained as far as possible at or near their point of origin in the fuel particles. The ceramic coated fuel particle concept is a promising means of minimising fission product release from the fuel element.

Some of the properties of ceramic oxides of interest as the coating material are compared with those of UO_2 , PuO_2 , and ThO_2 in Table 1. Physical properties are taken from Arthur (3,4) and cross section data from General Electric (5). Beryllia coatings are most desirable since no moderator is displaced by using it as the coating material, and it has a higher thermal conductivity than the other oxides. Alumina shows promise on the basis of these properties. The main disadvantage of magnesia is its high thermal expansion coefficient which gives rise to stresses in the coating, since the coating contracts more than the fuel particle on cooling from the coating temperature. A general requirement

TABLE 1
CERAMIC OXIDES FOR COATING FUEL PARTICLES

Oxide	Crystal Form	Melting Point °C	Average coefficient of Linear Expansion 20-1000 °C x 10 ⁶ /°C	Thermal Conductivity at 1000 °C 10 ⁻² cal/(cm)(sec)(°C)	Thermal Neutron Absorption Cross Section for the Metal barns
Al ₂ O ₃ *	Hexagonal	2050	8.5	1.5	0.23
BeO *	Hexagonal	2450	8.6	7.0	0.010
MgO *	Cubic	2800	13.7	1.6	0.03
SiO ₂	(Fused)	1713	0.55	-	0.1
ZrO ₂ *	Cubic	2680	10.3	0.55	0.1
ThO ₂	Cubic	3300	9.1	0.71	7.5
UO ₂	Cubic	2730	10.4	0.82	108 (for U235)
PuO ₂	Cubic	2280	11.4	-	300 (for Pu239)
* Coatings of this oxide have been deposited at the Battelle Memorial Institute, U.S.A. Blocher et al. (6).					

for a dense coating is a high coating temperature. Silica and zirconia are less suitable for use as the coating material since they are subject to phase changes, and have lower thermal conductivities and/or higher thermal neutron cross-sections than beryllia and alumina.

Processes available for depositing oxides as coatings on particles include -

- (1) applying a thick layer of sinterable ceramic powder to the particles by a "roll-up" method, then sintering (7,8),
- (2) coating by chemical vapour deposition, for example, deposition of an oxide by the hydrolysis of a suitable halide at the surface of the particles (9),
- (3) precipitation from a fused salt melt, for example, beryllia coated UO_2 particles produced by the reaction of steam with a molten salt mixture of UF_4 - LiF - BeF_2 (10),

The last method has not been used successfully for the preparation of coated particles of the required size, but information is available concerning the successful use of the other methods.

Chemical vapour deposition has been defined as the deposition of elements or compounds in massive form or as coatings, by chemical reaction of the vapours of suitable

compounds, usually at a heated surface (11). The technique has also been called gas plating, vapour plating, vapour phase metallurgy, molecular deposition, and vapour deposition (12). The term chemical vapour deposition is preferable to distinguish this method from physical vapour deposition processes such as vacuum evaporation. One of the advantages of chemical vapour deposition is that deposits are built up on an atomic or molecular scale, and the possibility of preparing materials of near theoretical density is inherent in the process. It therefore appeared likely that dense coatings produced by this method would have better fission product retention characteristics than could be expected with sintered coatings.

In this study, the technique of chemical vapour deposition in a fluidised bed, developed at the Battelle Memorial Institute, U.S.A., has been used to prepare coatings of beryllia and alumina and to establish the best conditions for coating deposition.

CHAPTER 2

REVIEW OF THE LITERATURE

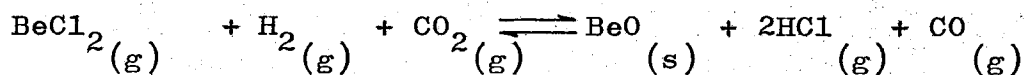
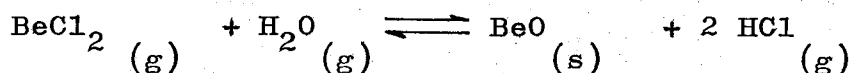
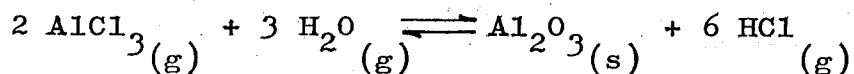
2.1 Preparation and Evaluation of Coated Fuel Particles

2.1.1 Methods of Chemical Vapour Deposition

Methods for depositing coherent coatings of metals, carbides, nitrides, boron, borides, silicon, silicides, and oxides by chemical vapour deposition techniques have been reviewed by Powell, Campbell and Gonser (13). Uranium and uranium dioxide particles have been coated with metals such as chromium, niobium, nickel, tungsten and molybdenum (14). The preparation of pyrolytic carbon coatings on uranium dioxide, and thorium and uranium carbides by the thermal decomposition of methane, acetylene, propane and naphthalene is also being extensively investigated (15, 16, 17, 18, 19, 20).

Considerable information is available on the oxide coating of uranium dioxide particles. Most effort has been devoted to alumina coatings by the Battelle Memorial Institute (BMI); less work has been carried out on beryllia, magnesia, and other oxide coatings. Reactions suitable for depositing oxides as coatings include

- (1) deposition of an oxide by hydrolysis of a suitable halide at the surface to be coated, for example (6)



- (2) thermal decomposition of a suitable organic compound at the surface, for example, basic beryllium acetate (6) to give beryllia coatings.

2.1.2 Methods of Particle Agitation

For any coating method, the particles must be maintained in relative movement during the coating operation to prevent agglomeration of the particles and assist in the uniformity of coating build-up. Methods which have been used include agitation in rotating (21) and vibratory drums (14); oscillatory pans (14), spiral beds (22), and fluidised beds (9). The rotating drum reactor and the oscillatory multipan reactor generally have a limited useful temperature range, and are suitable only for coatings produced at low temperatures. In the spiral bed apparatus, the reacting gases entered the wall of the reacting chamber tangentially and the fuel particles were caused to spiral upward. The velocity of the spiralling gases decreased as the hydraulic diameter of the chamber increased with height, and this permitted the

particles to fall from the gas stream. Thus, the particles passed repeatedly through the reaction chamber. The "fluidising efficiency" of the bed was stated to be quite high.

Nuclear Materials and Equipment Corporation (NUMEC) (14) claimed the vibrated horizontal drum reactor was superior to the fluidised bed reactor because

- (1) scale up to larger sizes is more easily achieved since agitation of the particles is produced mechanically, and therefore is independent of the gas flowrate required for fluidisation,
- (2) gas flowrates sufficient for the purposes of the chemical reactions involved in the coating process are required with no regard to agitation of the bed,
- (3) apparatus can be fabricated from metal and is therefore more rugged, shock-proof, and safer in operation than glass, silica, or ceramic fluidised beds.

In the preparation of oxide coatings it is questionable whether this last reason is justified since operation in the range 1,000 to 1,400°C in the presence of the corrosive atmospheres involved in chemical vapour deposition reactions almost certainly forces the use of a ceramic material for construction of the equipment, irrespective of the type involved. Large gas flowrates are involved in the use of

large fluidised bed installations, but recirculation of the inert fluidising gas required with the fluidised bed technique could be used, if it was economically justified. It should be noted that for the coating of enriched uranium dioxide particles, criticality considerations limit the diameter of the fluidised bed to about 5 inches (23).

A comparison of the efficiency of operation of vibratory drum and fluidised bed reactors using available data for niobium and molybdenum coatings (14, 24) shows that in a fluidised bed reactor 40 to 90 per cent of the metal fed to the reactor as chloride was deposited as coating on the particles, compared with 5 to 25 per cent for the vibratory drum reactor. The difference in performance is related to the effect of the larger free space in the reaction zone of the vibratory drum reactor, compared with that of the fluidised bed reactor. The operating efficiency of the fluidised bed reactor thus appears superior to that of the vibratory drum reactor.

2.1.3 Evaluation of Coated Particles

Coated particle properties have been evaluated by the following methods (25):

- (1) Metallographic examination by light and electron microscopy, and X-ray diffraction techniques.
- (2) Leaching in hot nitric acid, and testing of oxidation resistance.

- (3) Measurement of alpha particle emission.
- (4) Heat treatment and thermal cycling of coated particles above the deposition temperature of the coating.
- (5) Measurements of compressive strength and hardness.
- (6) Chemical analysis.
- (7) Neutron activation and post-irradiation heating.
- (8) Long term irradiations with high neutron doses.

In evaluation tests it is important to distinguish, if possible, between the total failure of one odd coated particle among many which perform well, and a slight general failure of all the coated particles. Uniformity of coating thickness and integrity is highly desirable to clarify the interpretation of these tests. Preliminary attempts at the impact testing of individual coated particles were made to develop a means of evaluating the integrity of every coated particle produced in a batch, but a successful technique was not devised (26).

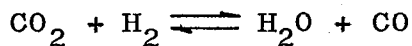
2.2 Alumina Coatings

2.2.1 Conditions of Deposition

Since 1959, BMI has developed the technique of chemical vapour deposition of alumina coatings by the hydrolysis of aluminium chloride in a fluidised bed. Operation of a fluidised bed for the coating of UO_2 particles has been discussed by Blocher et al (24), who denoted the "optimum level of fluidisation" as the condition when the maximum bed height was about four reactor diameters above the static

bed height. Typical operating conditions for coating deposition were given by Browning et al (9). Up to 95 per cent of the chloride was converted to the oxide in the reactor, and a maximum of 75 per cent of the alumina formed deposited as coating, the rest becoming entrained dust. Coating rates of 1 to 4 microns per hour have been reported. Fluidised bed reactors up to 5 inches in diameter have been used, and coatings up to 150 microns thick have been applied to UO_2 particles in the size range 44 to 350 microns in diameter (9,23). Spherical UO_2 particles have been used for most of the coating studies, but no difficulties have been experienced with angular particles (23) or with $(U,Th)O_2$ particles (27).

The water vapour required for the hydrolysis reaction may also be generated by the water-gas reaction, which is strongly temperature dependent.



This method has been used successfully (28,29) for coating beryllia tubes with alumina above $1100^{\circ}C$ and it was shown that the process gas composition and the operating variables, temperature and Reynolds number, affected the nature of the coating produced. Initial work at $1,000^{\circ}C$, using this reaction for the alumina coating of UO_2 particles gave incomplete hydrolysis of the aluminium chloride vapour (9), suggesting that for the chloride rate used the water vapour production

rate was too low. Subsequently satisfactory coating conditions were obtained at a temperature of $1,400^{\circ}\text{C}$ (30).

Some fine UO_2 dust, produced by the initial attrition of the UO_2 particles during fluidisation before the alumina coating is applied and by the occasional fracture of particles during the coating process, may subsequently be included in the coating during the deposition process. Uranium contamination of the coatings has been reduced to less than 10^{-6} of the contained uranium, that is, the uranium of the particle which is coated, as determined by alpha-counting techniques. This was achieved by stopping the coating process after 3 to 6 microns of alumina had been deposited, and rinsing the coated particles in nitric acid. The coating process was then recommenced in a clean reactor (9).

2.2.2 Structure and Properties

Coatings deposited at 500 to 700°C were porous, of low density, and amorphous in structure or possibly contained gamma- and kappa-alumina. Above 900°C , coatings became more translucent and dense, and showed the presence of alpha-alumina crystallites (6). Alumina coatings deposited at 1000°C were translucent, of near theoretical density, and consisted of small crystallites of alpha-alumina, with an average size of 0.3 microns, dispersed in an amorphous matrix. Coatings deposited at 1400°C were highly crystalline with an average crystallite size of 25 microns, transparent, dense,

void-free, and apparently consisted of columnar grains, with grain boundaries extending from the UO_2 substrate to the coating surface (31,32).

The temperature of deposition was the most important variable in determining the nature of the coating produced. The coating rate and the nature of the substrate also had an effect (6,33); for example, a 1000°C coating deposited over an amorphous alumina layer did not show the same degree of crystallinity as a 1000°C coating deposited over a highly crystalline coating (31). Little information is available concerning coating rate, but Blocher (23) reported that there was no apparent difference in the microstructure of coatings deposited at 4 microns per hour and at lower rates.

Heat treatment of coatings produced at temperatures in the range 500°C to 900°C gave a more crystalline structure, but a coating deposited at 1000°C was more crystalline than one heat-treated at 1000°C . Heat treatment of coatings deposited at 1000°C gave rise to increased crystallite size (31). Some experimental work has been carried out on the co-deposition of magnesium oxide as a grain growth inhibitor in alumina coatings, in an attempt to produce coatings capable of being heated above 1400°C , without grain growth and the associated loss of coating strength and integrity, for incorporation in oxide matrices. A concentration of 1.4 per cent magnesia in coatings prepared at 1025°C did

not significantly affect the grain size of the as-deposited or heat-treated material, but 3.1 per cent magnesia in a coating prepared at 1400°C decreased the grain size. After heat treatment for 15 hours at 1500°C in hydrogen, the grains of both doped and undoped coatings had grown to 10 and 25 microns respectively, that is, the maximum grain size in the doped coating was significantly less than in the undoped material (33).

Coatings deposited at temperatures in the range 1000°C to 1225°C exhibited a radially oriented alpha-phase alumina structure with the crystallographic a-axis nearly coinciding with the radial axis of the substrate particle. For coatings deposited at 1400°C , a different orientation has been observed in some coatings in which the crystallographic c-axis nearly coincided with the radial axis of the particle (31).

Coatings deposited at 1000°C have shown marked surface protrusions when produced in both the fluidised bed and the vibrating drum reactors (27). Coatings deposited at 1400°C showed much fewer surface protrusions than the 1000°C coatings (31). It has also been observed that coatings with the highest silicon and magnesium impurity content have the smoothest surface (34). Surface protrusions are undesirable since they result in stress concentrations in the coating during fabrication, which may lead to coating fracture. Attempts to minimise the growth of surface

protrusions at 1000°C by interrupting the growth pattern of the coating with a thin layer of amorphous alumina deposited at a lower temperature were successful. Coating integrity was however, adversely affected, as determined by air oxidation and acid leaching (31).

The hardness of coatings produced at 1000°C and 1400°C was equal to that of sapphire, but the crushing strength of UO_2 particles coated at 1400°C was only half that of 1000°C coated particles for the same coating thickness (30), presumably because of the weakness of the radial grain structure of the 1400°C coatings. Evaluation of the integrity of 1400°C coatings based on acid-leach data of heat-treated, air-oxidised, or as-produced materials showed that the coating integrity was inferior to that of a typical 1000°C coating (31).

The mechanism and kinetics of oxidation of spherical UO_2 particles coated with alumina were studied by thermogravimetric techniques (35,36). At temperatures below 1500°C , oxidation of the coated particles occurred by diffusion of oxygen through the coatings, partial oxidation to U_3O_8 , and subsequent cracking and complete oxidation. Tensile stresses in the coatings due to the difference in thermal expansion of urania and alumina were observed not to be responsible for coating failure during oxidation at

temperatures above the coating deposition temperature, even though Dayton and Tipton (31) reported that the annealing temperature for alumina coatings deposited on UO_2 particles at 1000°C was limited to 1250°C , previous evaluation tests having indicated that cracking occurred at higher temperatures. Oxidation resistance of UO_2 particles coated with alumina at 1300°C and 1400°C was superior to that of particles coated at 1000°C .

2.2.3 Fission Product Retention Characteristics

Three types of experiments have been carried out with alumina coatings on UO_2 particles:

- (1) neutron activation experiments in which the escape of xenon-133 is measured out of pile at temperatures above 1000°C , after a short irradiation period,
- (2) post-irradiation measurements of the release of xenon-133 recoiled into single crystal alumina during neutron irradiation in contact with UO_2 powder,
- (3) irradiation tests using static and sweep capsules.

In neutron activation experiments, UO_2 particles coated with 40 microns of dense alumina, which had passed the preliminary evaluation tests, showed xenon-133 release fractions at 1300°C in the range 10^{-5} to 10^{-9} (9,37). This was of the same order as the uranium contamination in the

coatings, and the xenon-133 was generally attributed to this source. It is generally inferred that no xenon-133 is released through the coating.

Post-irradiation measurements of the release of xenon-133 recoiled into single crystal alpha alumina during neutron irradiation in contact with UO_2 powder were made in the temperature range 500 to 1500°C (38). The initial release of xenon-133 during the post-irradiation heat treatment was very rapid, giving rise to a burst. After several minutes, the release rate decreased, and the variation of cumulative fraction release with heating time indicated a diffusion-controlled process. The activation energy calculated from the temperature dependence of the diffusion coefficients for this release was 64 ± 18 kcal per gram mole for an exposure of 3×10^{13} fission recoils per cm^2 of surface area in the range 1040 to 1550°C . An activation energy of 9.2 ± 2 kcal per gram mole was calculated for diffusion below 1040°C at this exposure. For higher radiation exposures up to 1.5×10^{18} fission recoils per cm^2 , only the higher activation energy process was observed.

Irradiation of UO_2 particles (127 micron average diameter) coated with 40 microns of dense alumina deposited at 1000°C in static and sweep capsule tests (39) indicated that dense as-deposited alumina coatings had essentially complete fission product retention at 1070°C for up to

3 per cent uranium burnup, with fission product release ratios (R/B) of better than 10^{-6} (release ratio = rate of fission product release divided by rate of fission product generation), but failed rapidly at approximately 100°C in a thermal neutron flux of $1 \text{ to } 2 \times 10^{13}$ neutrons $(\text{cm})^{-2}(\text{sec})^{-1}$. Failure was essentially complete in a few hours. This low temperature failure occurred only at temperatures below 500°C . Composite coatings of dense and porous alumina layers did not significantly reduce low temperature failure, or provide the same degree of fission product containment at elevated temperatures as was obtained with fully dense coatings. Annealing of dense alumina coatings did not improve their low temperature behaviour. Coated particles supported in graphite matrices behaved similarly to unsupported coated particles, although some of the fission products were retained in the matrix at low temperatures. Recent irradiation results suggested that thicker coatings on relatively porous UO_2 particles (less than 92 per cent theoretical density) gave better performance at low temperatures.

Low temperature failure of alumina coated UO_2 particles has been attributed to radiation damage. Oxley and Townley (33) suggested that radiation induced expansion of the UO_2 particle was a major cause of failure, but fission recoil induced strains (40,41) in the coating and the buildup of fission gas pressure within the coating could also be

significant contributing factors. Above 500°C, annealing of some of the damage was assumed to be sufficient to prevent cracking.

Currently work at the Battelle Memorial Institute is directed towards the preparation of coated particle specimens with composite coatings intended to resist fission recoil damage, permit substrate swelling and the accumulation of fission gases, and limit crack propagation. Coatings incorporating various combinations and selections of porous and dense alumina, beryllia, and pyrolytic carbon layers on dense and porous UO_2 particles are being evaluated.

2.3 Beryllia Coatings

Beryllia coatings on UO_2 particles have been produced by the hydrolysis of beryllium chloride, and the decomposition of basic beryllium acetate, in equipment similar to that used for the deposition of alumina coatings.

2.3.1 Coatings Deposited by the Hydrolysis of Beryllium Chloride

Coatings prepared by the hydrolysis of beryllium chloride at 700 to 1100°C, if uncontaminated by impurities from the beryllium chloride or corrosion products from the fluidised bed reactor, have been porous (densities as low as 40 per cent of the theoretical) with a spiny surface in thicknesses above twenty microns. Only coatings contaminated with 0.1 to 2 per cent silicon or aluminium have been relatively smooth, dense, and transparent (6).

Coatings deposited at 1400°C have been translucent, dense, and of low porosity when deposited by either direct water vapour hydrolysis or the use of the water-gas reaction (42). The coatings consisted of small crystallites of beryllium oxide in an amorphous matrix of the same material. The crystal size was shown to be related to the coating purity. Coatings with total impurity contents of several thousand ppm had a fine grain structure of crystals mostly in the size range 2 to 10 microns; a highly pure coating was composed of crystals up to 70 microns along the c-axis. Knoop hardnesses equal to that of high fired beryllia (1300 to 1500 kg/mm²) have been obtained (43). The water vapour/beryllium chloride feedrate ratio had no significant effect on coating properties in the range 0.5 to 1.5 (30).

Beryllia coatings deposited at 1500°C had smooth surfaces and consisted of large grains often equal to the coating thickness (44). This large grain size is considered to be undesirable because of the anisotropy of radiation damage in beryllium oxide. Fine grain-size beryllium oxide has been shown to withstand much higher doses of neutron irradiation without micro-cracking than coarse grain material (45). Furthermore, out-of-pile tests also suggested that large grain coatings of alumina and beryllia are inferior to those of a fine grain structure (44).

Coatings deposited at 950°C were cryptocrystalline in structure (31), while coatings deposited at 1400°C were highly crystalline with a radial grain structure, the crystallographic c-axis generally coinciding with the radial direction of the particle, that is, the growth direction. Crystal orientation was less apparent for coatings deposited at lower temperatures (46).

Acid-leach and air-oxidation tests have shown the best beryllia coatings obtained so far to be inferior to good alumina coatings. This has been attributed to general porosity in the beryllia coatings rather than to cracks or failure of a fraction of the coatings (42), but recent data (43) indicated that the impurity content of the coatings may have a significant effect. Coatings with less than 200 ppm calcium and 500 ppm silicon contamination have shown best acid-leach resistance, but no significant correlation with aluminium content has been observed. Nonuniformity of coating thickness and uranium contamination in the coatings have also been problems with beryllia coatings. The cause of these difficulties has not yet been defined (33).

It was considered possible that an intermediate product, beryllium hydroxide, was formed by the hydrolysis of beryllium chloride, and that this might be the cause of porosity in the beryllia coatings. To overcome this, the direct oxidation of beryllium chloride was investigated. The

reaction rate was found to be negligible at 1000°C , and at 1400°C was increased by only one order of magnitude. No further use was made of this reaction (31).

2.3.2 Coatings Deposited by the Thermal Decomposition of Basic Beryllium Acetate

Beryllia coatings prepared by the thermal decomposition of basic beryllium acetate in hydrogen from 500 to 900°C have been contaminated with 2 to 8 per cent carbon (6,47). These coatings were transparent and glassy smooth, with apparently high densities. The presence of 10 mole per cent water vapour in the reactant atmosphere greatly increased the deposition rate at 500°C , but oxidation of part of the UO_2 was observed. Coatings prepared by the basic beryllium acetate method have released varying quantities of water vapour when heated in vacuum at 500°C , and have shown varying solubility in nitric acid. Attempts to prepare beryllia coatings at 1400°C by this method have been unsuccessful due to premature decomposition of the acetate which caused blockages in the reactor (42).

2.3.3 Fission Product Retention Characteristics

Only limited data are available for the radiation testing of beryllia coated UO_2 particles. UO_2 particles (average diameter 127 microns) coated with 60 microns of dense beryllia failed rapidly during irradiation at 100°C (32). When irradiated at 900°C , fission product release ratios (R/B) were in the range 10^{-8} to 10^{-7} indicating no failure, after nearly

3 per cent burnup of the uranium (33). Beryllia coatings appear to perform in the same manner as alumina coatings with good performance at elevated temperature but rapid failure at low temperature.

2.4 Mechanism of Coating Buildup by Chemical Vapour Deposition

Little information is available concerning the mechanism of coating buildup using chemical vapour deposition techniques. In general, it is assumed that both a heterogeneous surface reaction giving rise to the coating and a homogeneous gas-phase reaction producing dust take place (32, 48, 49). In the alumina coating of beryllia tubes however, Van Houten et al (28) reported that the reaction was apparently a gaseous phase, non-surface catalysed reaction. Just how nucleation and crystal growth occur as a result of the various chemical reactions is not understood.

Assuming a heterogeneous surface reaction gives rise to the coating, the mechanism of coating buildup may be explained by classical nucleation and growth theory (50) in which growth apparently occurs more readily at kinks and step sites than on smooth crystal planes. Thus the growth of a crystal could result from

- (1) the transport of the reactant molecules from
the vapour phase to the adsorbed state on
the surface,

- (2) migration of surface adsorbed species to kinks and step sites, (the migrating species could be either the reactant molecules, molecules of intermediates in the overall deposition reaction, or molecules of the final product).
- (3) accretion of product molecules at growth sites to give a growing crystal.

The surface reaction between the reactant molecules could occur either in the initial adsorbed positions or at the growth sites. The presence of dislocations, for example, a screw dislocation generated by an impurity atom which has been engulfed by a growing layer, would enable steps to advance indefinitely without necessarily requiring the nucleation of new layers (48).

Dayton et al (32) suggested that porous coatings were deposited at low temperatures perhaps because the oxide nucleated in the gas phase and subsequently attached itself to the surface of the fuel particles, or possibly owing to the deposition of intermediate products such as oxyhalides or hydrated oxides which were subsequently converted to the oxide with corresponding density changes. At higher temperatures, it was postulated that either the gas phase nucleation tendency was reduced as a result of a shift in the reaction equilibrium, or the intermediate products did not form, or the material recrystallized quickly, so that

dense coatings were obtained. The microcrystallinity of dense vapour deposited alumina coatings has been attributed to the large number of growth sites formed by the frequent energetic collisions of the particles in the fluidised bed (27).

CHAPTER 3AIM OF THIS INVESTIGATION

When the present investigation was begun in late 1961, much of the information presented in Chapter 2 had not been published. However, the promise of alumina coated UO_2 particles had been established (9,51) and work had begun on the preparation of beryllia coated UO_2 particles. In general, a systematic study of the variables in the coating of fuel particles had not been carried out. Work at BMI had apparently consisted of a limited study of the effect of coating conditions on coating properties, and the preparation of specific coated particle specimens for irradiation testing. The latter aspect had received the major emphasis.

For this study to be a contribution to the rapidly expanding field of research into coated particles, it was recognised that effort should be devoted to the systematic investigation of the variables affecting coating deposition in an attempt to optimise coating properties. This implied a study of the effects on coating properties of variables such as reactant feedrate ratio and coating rate, which had apparently been neglected by other workers.

The technique of chemical vapour deposition in a fluidised bed was chosen as the most promising method of coating

deposition, and the hydrolysis of aluminium chloride and beryllium chloride with water vapour were selected as the reaction systems. The deposition of alumina coatings was first investigated and subsequently beryllia coating conditions were studied. Preliminary coating runs were made using $(\text{U,Th})\text{O}_2$ fuel particles, but UO_2 particles were used for most coating runs since evaluation of the coatings by acid-leach and air-oxidation testing was more readily performed in this case. The kinetics of the hydrolysis reactions and the behaviour of the fluidised bed were of interest only in so far as they influenced the conditions of coating deposition.

CHAPTER 4

PREPARATION AND EVALUATION OF COATED PARTICLES

4.1 Supply of Feed Materials

The fabrication of sintered UO_2 and $(\text{U,Th})\text{O}_2$ fuel particles with a density greater than 95 per cent of the theoretical, is described in Appendix I.

The preparation of beryllium chloride required for the beryllium oxide coating studies is described in Appendix II. Beryllium chloride obtained from Brush Beryllium Co. was also used in this work. Laboratory grade anhydrous aluminium chloride was used for the alumina coating studies.

4.2 Equipment

4.2.1 Low Temperature Units

The apparatus used to coat particles of UO_2 and $(\text{U,Th})\text{O}_2$ with alumina and beryllia at temperatures up to 1100°C was essentially the same as that reported by Browning et al (9). Figure 1 is a schematic diagram of the coating apparatus. Because of the toxicity hazards associated with the use of beryllia and uranium and thorium oxides, the equipment was located in glove boxes maintained at 1-inch water pressure below atmospheric conditions. Figures 2 and 3 are photographs of the equipment used for the alumina and beryllia coating studies. The glove box used for the beryllia coating work included facilities for the cleaning and decontamination of

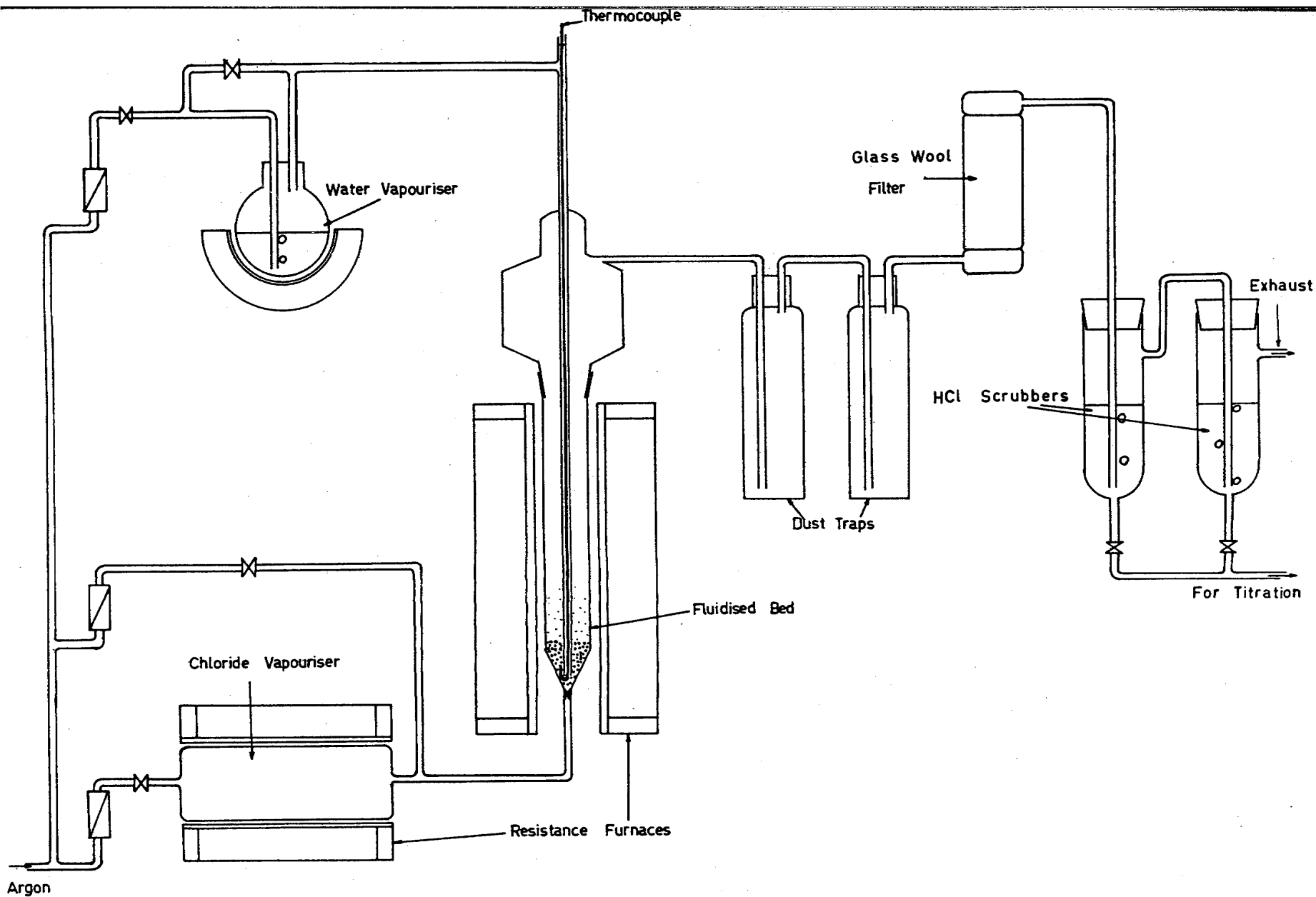


FIGURE 1. SCHEMATIC DIAGRAM OF THE LOW TEMPERATURE COATING APPARATUS

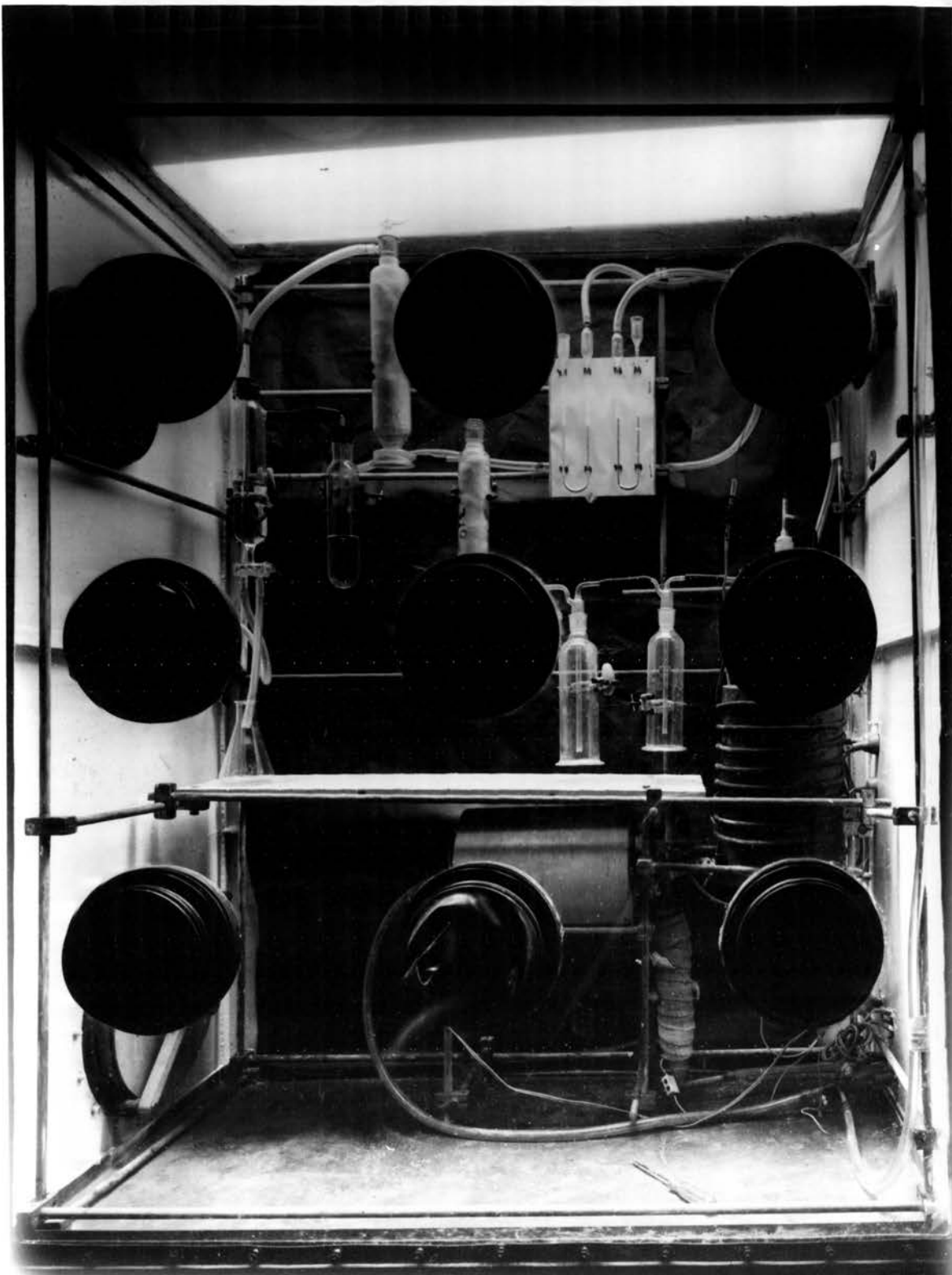


Figure 2 - Photograph of the Alumina Coating Apparatus

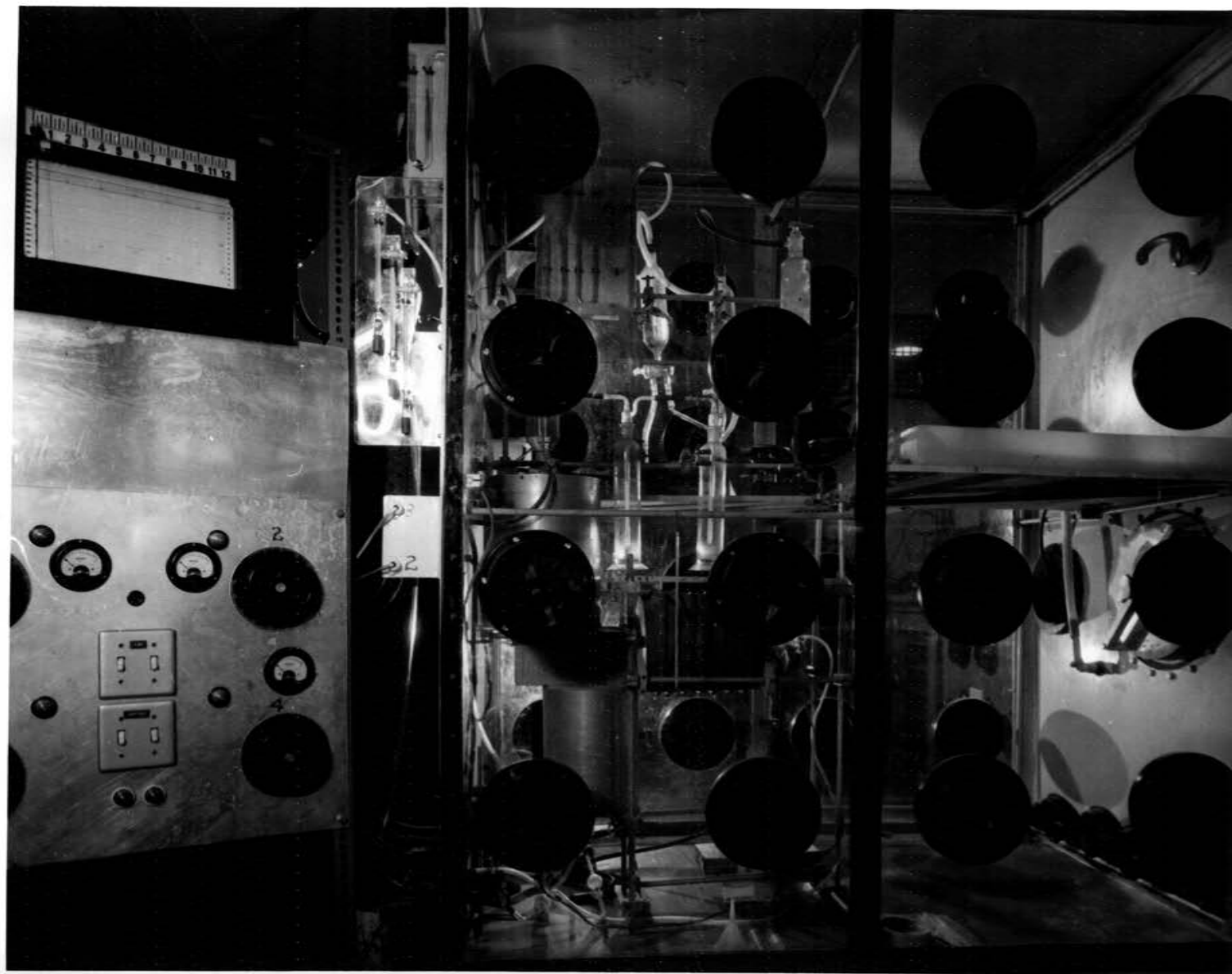


Figure 3 - Photograph of the Beryllia Coating Apparatus

equipment items, but the alumina coating equipment could be removed from its glove box for cleaning.

The fluidised bed reactor consisted of a 30 mm vycor tube with a conical bed support and a 2 mm restriction at the bottom of the bed. The argon fluidising gas and the chloride vapour were introduced into the reactor at the bottom of the bed, and the water vapour was carried into the bed with an argon carrier gas through a vycor tube extending from the top of the reactor. The reactants were introduced separately to prevent premature hydrolysis, and mixing occurred in the fluidised bed. A disengaging space at the top of the reactor minimised loss of fuel particles from the bed. Dust traps and glass wool filters removed alumina dust from the exit gas stream. The hydrogen chloride produced in the hydrolysis reaction was scrubbed from the exit gas in a water absorber, before it discharged to the ventilation system.

The fluidised bed and the chloride vapouriser were heated by nichrome wound resistance furnaces, and their temperatures controlled by reference to chromel-alumel thermocouples. The fluidised bed temperature was measured with a stainless steel clad thermocouple exposed to the reaction conditions and inserted into the fluidised bed through the water vapour inlet tube. The water vapouriser was heated by a resistance heating mantle and the temperature measured with a thermometer.

Argon was metered to the water vapouriser, chloride vapouriser, and the fluidised bed reactor. Non-return valves were provided in these lines. Manometers for determining pressure drops throughout the system were included. The line from the chloride vapouriser to the fluidised bed reactor was heated with a resistance heating element to prevent condensation of the chloride in the line. Trace heating was used with the alumina coating equipment and a "hot finger" was employed with the beryllia coating apparatus.

4.2.2 High Temperature Unit

Initial beryllia coating runs at 1400°C were made using equipment similar to the low temperature unit, with a fluidised bed reactor consisting of a 30 mm I.D. alumina tube with a cast conical bed support of alumina cement (cone angle 57°). The performance of this equipment was unsatisfactory since approximately 30 per cent of the UO_2 particles charged to the fluidised bed agglomerated owing to poor fluidisation.

Figure 4 shows the equipment subsequently used for coating UO_2 and $(\text{U,Th})\text{O}_2$ particles with beryllium oxide at 1400°C . It was located in the same glovebox used for the low temperature beryllia coating studies when that work was completed. The apparatus was made up of a static bed beryllium chloride producer and a fluidised bed coating reactor. The beryllium chloride was prepared in situ by the chlorination

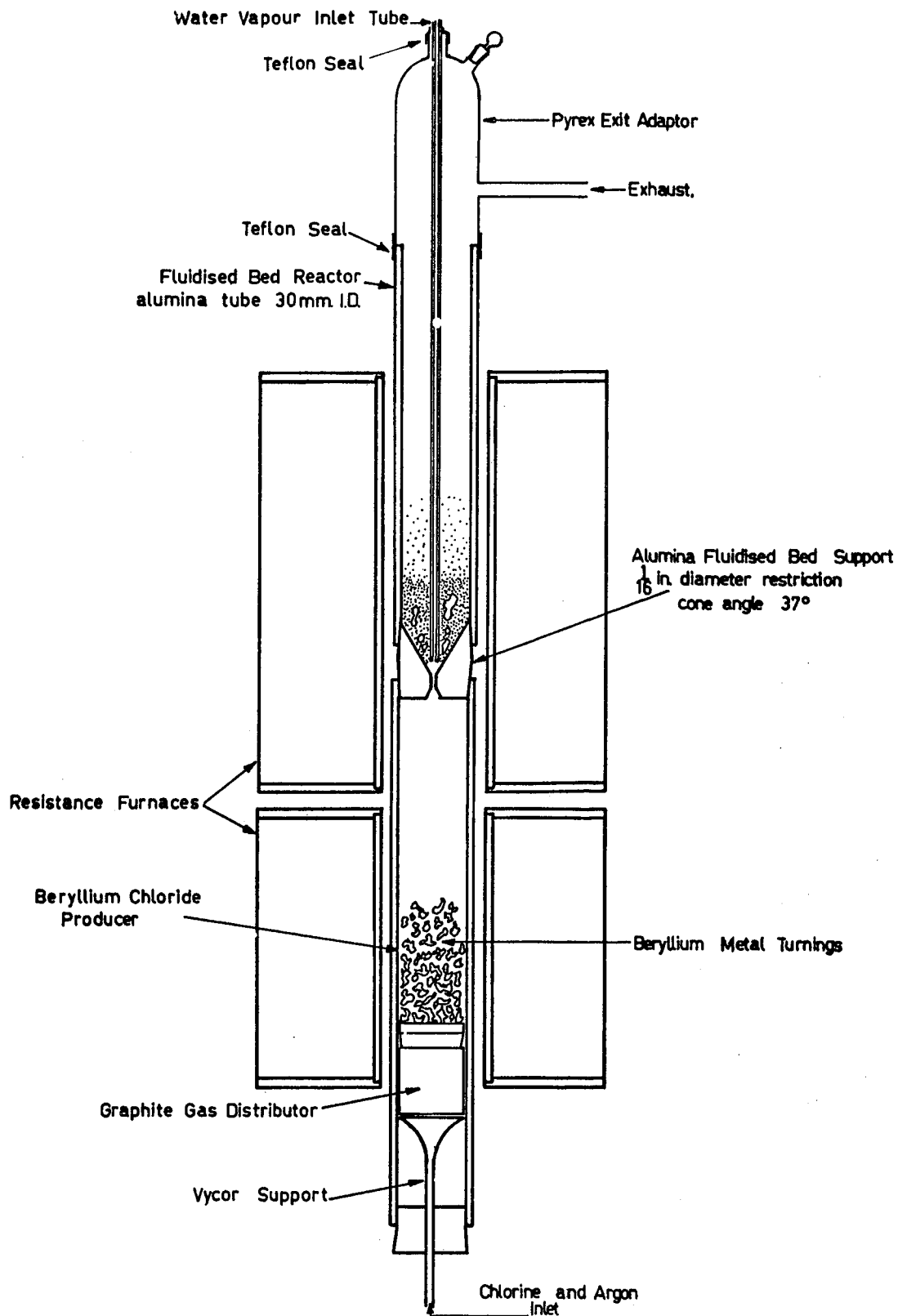


FIGURE 4. SCHEMATIC DIAGRAM OF THE HIGH TEMPERATURE COATING APPARATUS.

of beryllium turnings and passed directly to the fluidised bed. The water vapour was carried into the bed with an argon carrier gas through an alumina tube extending from the top of the reactor.

The beryllium chloride producer consisted of a 30 mm I.D. alumina tube, sealed at the bottom with a neoprene rubber stopper, and a graphite gas distributor resting on a vycor bed support. The beryllium chloride producer was heated with a nichrome resistance heater controlled by reference to a chromel-alumel thermocouple between the reactor wall and the furnace former. Chlorine and argon were fed into the bottom of the bed and the beryllium chloride passed to the fluidised bed reactor above.

The fluidised bed reactor consisted of a 30 mm I.D. alumina tube connected to the beryllium chloride producer by a cast alumina connecting piece which formed the bed support for the fluidised bed reactor. A cone angle of 37° was used since, at 1400°C , a 57° cone gave unsatisfactory fluidisation in initial runs and Browning et al (20) had reported a 37° cone to be superior to a 57° cone in the pyrolytic carbon coating of UO_2 and UC_2 particles.

The coating reactor was heated with a molybdenum wound resistance furnace, after a platinum wound furnace proved unable to operate consistently at 1400°C . A blanket gas of 3 per cent hydrogen in nitrogen was used to protect the furnace winding. The fluidised bed temperature was measured

with a platinum - platinum 13 per cent rhodium thermocouple positioned for convenience between the reactor wall and the furnace former. A check at 1400°C against a thermocouple immersed in the bed showed that the latter gave a reading 10°C lower than did the outside thermocouple. This temperature difference was not significantly affected by variations in the fluidising gas velocity within the range of interest in this work.

4.3 Procedure

4.3.1 Low Temperature Unit

The apparatus was assembled and leak tested after weighing the chloride vapouriser and the water vapouriser. The fluidised bed reactor was then heated to the coating temperature. As the operating temperature was approached, a weighed quantity of fuel particles was added, the bed being fluidised with argon. Both vapourisers were then heated to their operating temperatures with no gas flow through the chloride vapouriser and the argon carrier gas bypassing the water vapouriser. When the fluidised bed reached the coating temperature, controlled flow of argon through the vapourisers was commenced. The progress of the hydrolysis reaction was followed by titrating the hydrogen chloride content of the water scrubber with a 3M sodium hydroxide solution at 10 minute intervals. The feedrates of the reactants were

controlled by adjusting the temperatures of the vapourisers. The water vapour feedrate was based on previous calibration against the vapouriser temperature, and the beryllium chloride feedrate was controlled on the basis of the titration of the absorbed hydrogen chloride.

When the coating operation was terminated, the gas flow to the vapourisers, and the power to all furnaces were shut off, but the fluidising gas was maintained. When cool, the apparatus was dismantled, and changes in weight of the fuel particles, chloride vapouriser, and water vapouriser were determined.

4.3.2 High Temperature Unit

About 10 g of beryllium turnings were added to the beryllium chloride producer, and the equipment was assembled and leak tested after weighing the water vapouriser. The fluidised bed reactor and the beryllium chloride producer were heated to their respective operating temperatures. The water vapouriser was also heated to its operating temperature with the argon carrier gas by-passing it. As the fluidised bed operating temperature was approached, a weighed quantity of fuel particles was added, the bed being fluidised with argon. When all equipment items were at the required operating temperatures, chlorine was passed to the beryllium chloride producer and argon gas flow through the water vapouriser was initiated. The water vapour feedrate was controlled by adjusting the temperature of the vapouriser, and the beryllium

chloride rate was controlled by the chlorine gas flow to the producer. The progress of the hydrolysis reaction was followed by titrating the hydrogen chloride content of the water scrubber with sodium hydroxide solution at 10 minute intervals.

When the coating operation was terminated, the chlorine flow to the beryllium chloride producer, the argon to the water vapouriser, and all furnaces and heaters were shut down. The fluidising argon gas stream was maintained. When cool the apparatus was dismantled and changes in weight of the fuel particles, beryllium turnings, and water vapouriser were determined.

4.4 Evaluation Tests

4.4.1 Metallographic Examination

Metallographic examination and X-ray diffraction analyses were carried out by the Physical Metallurgy Group at the A.A.E.C. Research Establishment. Coated particles were mounted in an araldite or cold-setting resin pellet which was incorporated in a bakelite mount. The specimen was metallographically polished, and examined microscopically up to 1000x to determine the coating integrity, thickness, uniformity, porosity, and penetration of the coating into the substrate. X-ray diffraction analysis was used for characterisation of the coating structure. The Knoop hardness

of the coatings was measured with a Leitz Durimet Micro-hardness Tester.

4.4.2 Chemical Analysis

Chemical analyses were carried out by the Analytical Chemistry Section at the A.A.E.C. Research Establishment. Standard analytical methods were used for determination of the composition of the coated particles. The weight fraction of coating material and the presence of silicon impurities in the coating were found using spectrophotometric techniques, and residual chloride ion in the coating was measured by a silver chloride turbidometric method.

4.4.3 Acid-leach Testing

Acid-leach tests of coated particles were made using 7.5 M nitric acid at 90°C. About 0.2 to 2 g samples of coated particles were leached with 10 ml of acid for an initial 6 hours to dissolve any uncoated particles, or particles with cracked coatings, and then leached for a second 6 hours to determine the general porosity characteristic of the coating. Initially leach tests were made without agitation, but most tests used agitated conditions. Acid leaching with agitation was carried out in vertically mounted sealed capsules rotating about a horizontal axis at 9 rpm. The leach solution was analysed for uranium, and dissolved coating material in some cases, by spectrophotometric methods.

Acid-leach testing of coated (U,Th) O_2 particles was also made using 7.5 M nitric acid containing 0.005 M sodium

fluoride, since traces of fluoride ion are needed to dissolve thorium.

4.4.4 Air Oxidation Testing

Alumina and beryllia coated UO_2 particles were weighed before and after heating at 1000°C in air for one hour to determine the integrity of the coating. If the coating was permeable to oxygen the uranium dioxide oxidised to uranium oxide U_3O_8 with a resultant volume increase which fractured the coating and allowed complete oxidation of the UO_2 particle. Subsequent acid-leach testing was used to confirm the failure of coatings. Air oxidation testing was not applicable to coated $(\text{U,Th})\text{O}_2$ particles.

4.4.5 Alpha Emission

The alpha emission from some coated particles with coating thicknesses greater than the range of alpha particles in the coating material, namely 12 and 10 microns for beryllia and alumina respectively, was measured to estimate the uranium contamination in the coatings. Approximately 0.2 g of coated particles was placed as a monolayer on a counting chamber tray, and the alpha emission from the coated particles was measured in a zinc sulphide scintillation counter. The background count was taken before and after each determination. From these measurements, uranium contamination in the coating was calculated assuming uniform distribution of the uranium

in the coating with no self-absorption of alpha particles, and allowing for the efficiency of the counter, and the absorption of alpha particles in the coating. Appendix III gives the derivation of a correction factor to allow for the absorption of alpha particles in the coating.

4.4.6 Heat Treatment

To demonstrate the effect of a heat treatment process similar to that required for fabrication of fuel specimens on the integrity of coated particles, samples of particles were heated in alumina trays at 1500°C in nitrogen for 2 hours, in a molybdenum wound sintering furnace. Heat treated samples were then evaluated by metallographic examination, etc.

4.4.7 Xe-133 Release on Post-Irradiation Heating

These measurements were made by Palmer and Whitfield (52). A sample of coated particles was sealed in an air filled silica ampoule and irradiated in a thermal neutron flux of $1 \text{ to } 2 \times 10^{13} \text{ nv}$ at approximately 100°C for the required time. The sample was then allowed to stand for 7 days to allow essentially all the iodine-133 to decay to xenon-133. The neutron activated sample was transferred to apparatus for measuring the xenon-133 released from the specimen when heated to temperatures in the range $900\text{--}1300^{\circ}\text{C}$. The xenon-133 gas released from the specimen was continuously

pumped off, separated from iodine and tellurium isotopes by a hot copper gauze trap, and condensed in a bed of molecular sieves Linde type 5A, cooled by liquid nitrogen. The trapped xenon-133 gas was continuously monitored with a scintillation counter and a single channel gamma spectrometer set to count xenon-133 selectively.

CHAPTER 5

RESULTS OF COATED PARTICLE STUDIES

5.1 Summary of Experimental Data

Tables 2, 3, 4, 5 and 6 in Appendix IV give a summary of the experimental data on the preparation and evaluation of the alumina and beryllia coated fuel particles.

A mass balance on the fuel particles was calculated as a percent of the particles charged to the bed, using data for the chemical analysis of the recovered coated particles as well as for uncoated particles, held up on the walls of the reactor and in the disengaging space by oxide dust. The mass balance was commonly less than 100 percent because of spillage of particles due to experimental difficulties in the dismantling of equipment within a glove-box. The percentages of particles charged to the fluidised bed which were recovered as coated particles are also shown.

The conversion efficiency of the hydrolysis reaction was calculated from the quantity of chloride reacted to produce the amount of hydrogen chloride absorbed in the water scrubbers relative to the feed of chloride to the fluidised bed.

The bed efficiencies reported give the weight of oxide deposited as coating as a percentage of that available in

the feed to the fluidised bed. Since complete recovery of the particles was not possible in every case, bed efficiencies could not be calculated from the increase in weight of the bed and therefore were calculated on the basis of the chemical analysis results for the recovered coated particles. In the cases where essentially complete recovery of the particles was achieved, check calculations of the bed efficiencies based on the increase in weight of the bed agreed satisfactorily with those reported in Tables 2 and 5. The bed efficiency may also be calculated from the thickness of the deposited coating, assuming a coating of theoretical density. This gives a maximum estimate for the bed efficiency and may be used as a further check on the efficiencies calculated by the other methods, although it is very sensitive to particle diameter and coating thickness especially for thin coatings. Table 7 gives typical results comparing the values of bed efficiency calculated by the three methods.

The rate of coating build-up was also calculated on the same bases. The rates reported in Tables 2 and 5 are based on chemical analysis of the recovered coated particles.

The Knoop hardness of the coatings is expressed as the mean $\pm$ standard deviation, based on 6 to 8 impressions per sample.

TABLE 7 - COMPARISON OF METHODS FOR
CALCULATING THE BED EFFICIENCY

Run	Bed Efficiency (%)		
	Based on increase in weight	Based on chemical analysis	Assuming 100% theor. density coating
A19-I	35	36	29
A20-I	34	33	33
A21-I	31	31	45
A22-I	31	33	32
A23-I	26	34	54
A24-I	25	25	22
A25-I	28	34	68
B9-I	33	33	35
B10-I	36	38	35
B11-I	34	32	34
B13-I	35	39	36
B14-I	30	42	50

Acid leaching results are reported as the percent of uranium, and thorium if applicable, dissolved relative to the amount of uranium and thorium as the oxides contained within the coating. Similarly, air oxidation results are expressed as the percent of UO_2 oxidised relative to the UO_2 contained within the coating. The extent of coating dissolution is given as a percent of coating material present, as determined by chemical analysis.

The presence of silicon and chloride ion impurities in the coating are expressed as parts per million by weight of the coating material. Uranium contamination in the coating is expressed as the percent of the substrate material indicated by alpha counting to be distributed in the outer thickness of the coating, equivalent to the alpha range in that material.

5.2 Results of Alumina Coating Studies

5.2.1 Conditions of Deposition

Sintered particles of $(\text{U,Th})\text{O}_2$ and UO_2 , with a density greater than 95 per cent theoretical, were coated with alumina at temperatures in the range 500 to 1100°C and coating rates of 1 to 20 microns per hour to give coatings up to 65 microns in thickness. Runs of up to 6 hours duration were made usually with a 50 gram bed of particles in the size range -72 +100 BSS, and an argon fluidising gas rate of approximately 2.8 litres per minute measured at STP.

Hydrogen was used by Browning et al (9) as the inert fluidising gas, but in this investigation argon was preferred for greater safety in glove box operation. Calculation of the minimum fluidising gas velocity, using the generalised equation given by Leva (53) and assuming the fluidising gas is heated to the bed temperature, indicated the hydrogen flowrate of 3.0 litres per minute used by Browning et al was 7 to 8 times the minimum fluidising gas flowrate required. The argon flowrate used in this work was calculated on the same basis.

Figure 5 shows the conversion efficiency of the hydrolysis reaction for a fluidised bed temperature of 1000°C as a function of the feedrates of the reactants. For a molar feedrate ratio of the reactants $\text{AlCl}_3/\text{H}_2\text{O}$ of 0.33 (which corresponds to 100 per cent excess water vapour based on stoichiometric requirements) or less, conversion efficiencies in the range 80 to 100 per cent were generally obtained. Lower conversion efficiencies were achieved with increased ratios of the reactants. The conversion efficiency decreased with increasing aluminium chloride feedrate, for $\text{AlCl}_3/\text{H}_2\text{O}$ ratios in range 0.28 to 0.38 (Figure 6).

Usually 30 to 40 per cent of the alumina fed to the fluidised bed as aluminium chloride was deposited as coating on the particles. The conversion efficiency of the hydrolysis reaction and the per cent of alumina deposited as coating were

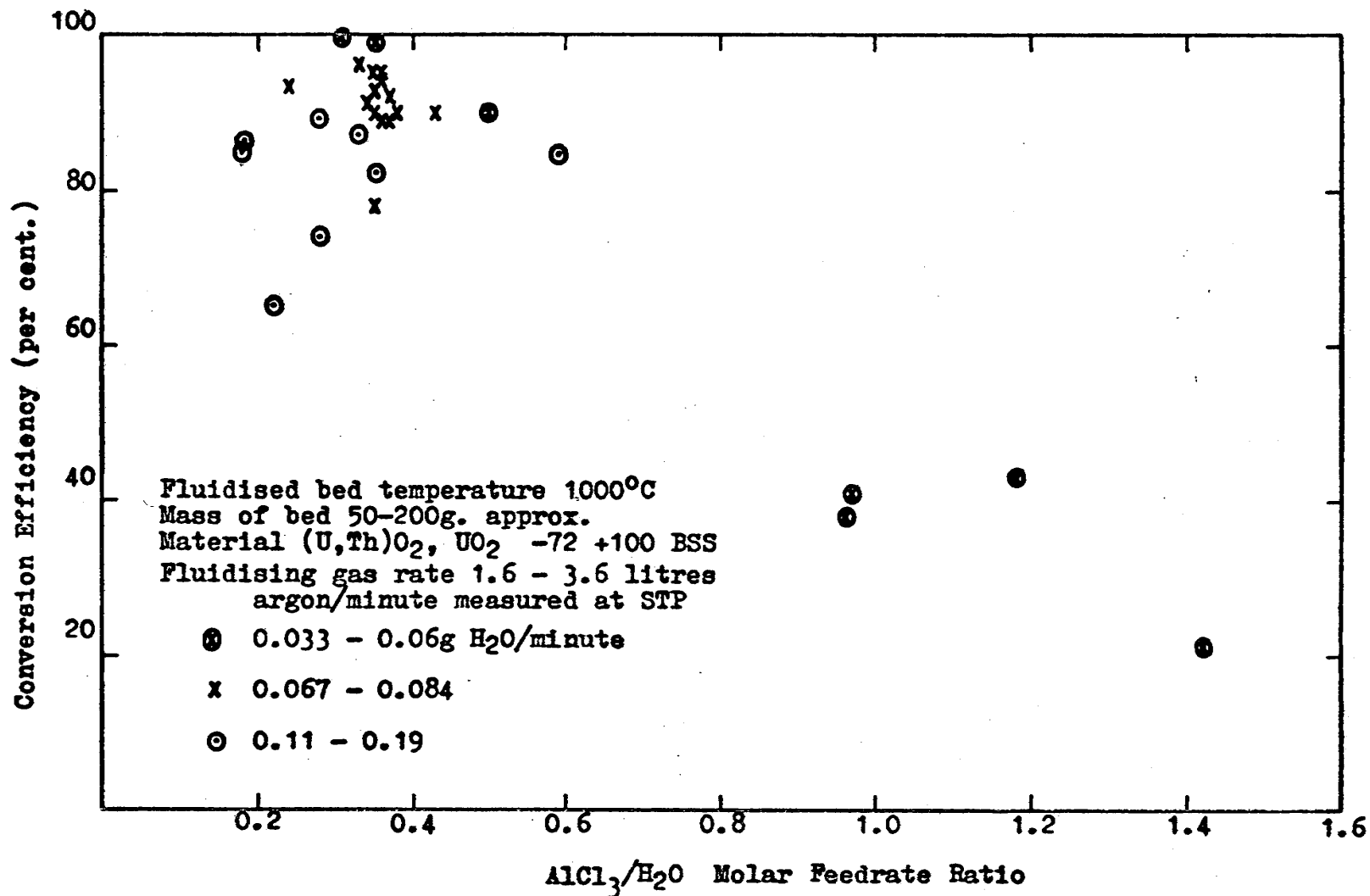


FIGURE 5 CONVERSION EFFICIENCY OF THE ALUMINIUM CHLORIDE HYDROLYSIS REACTION -
 EFFECT OF REACTANT FEEDRATE RATIO

Fluidised bed temperature 1000°C
 Mass of bed 50g. approx.
 Material (U,Th)O₂, UO₂ -72 +100 BSS
 Fluidising gas rate 1.6 - 3.6 litres argon/minute
 measured at STP
 AlCl₃/H₂O ratio 0.28 - 0.38

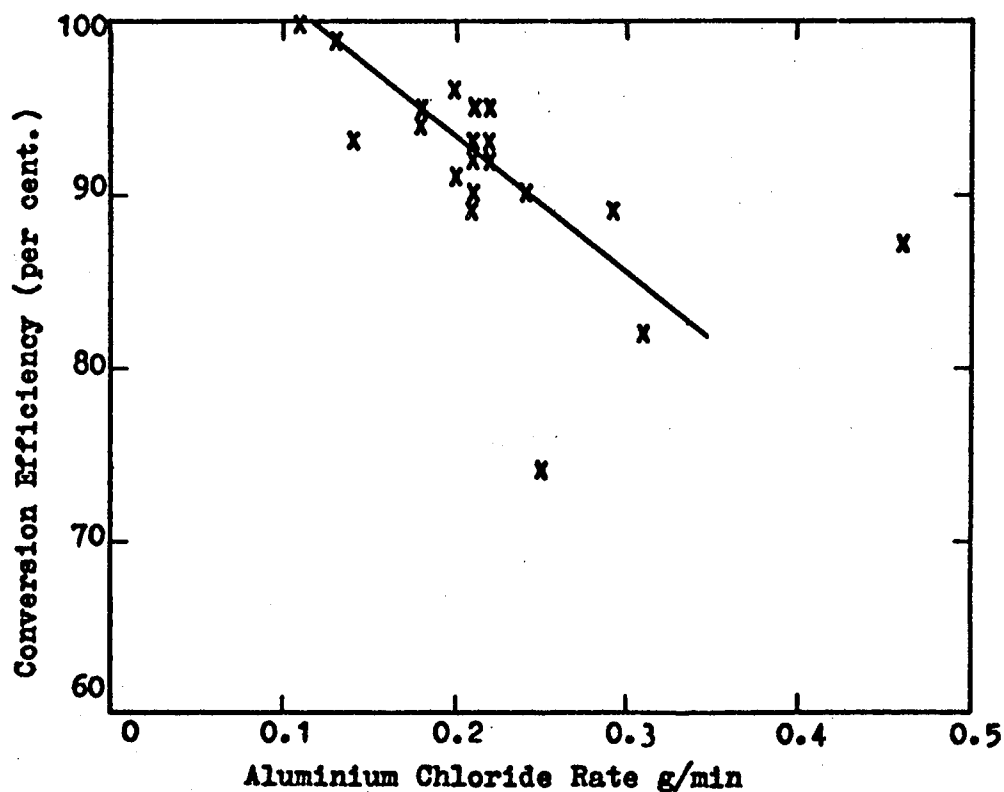


FIGURE 6 CONVERSION EFFICIENCY OF THE ALUMINIUM CHLORIDE HYDROLYSIS REACTION -
 EFFECT OF ALUMINIUM CHLORIDE FEEDRATE

only slightly affected by using beds of particles in the size range 50 to 200 grams. Variation in particle size, in runs where coatings were built up in a number of steps to about 40 microns in thickness, had no effect on the performance of the fluidised bed. Figures 7 and 8 are graphs of data which suggest that the bed efficiency and the conversion efficiency of the aluminium chloride hydrolysis reaction decreased with increasing fluidising gas flowrates. The lines drawn through the data have been fitted by the method of least squares, taking the fluidising gas flowrate as the independent variable.

The conversion efficiency of the hydrolysis reaction increased with increasing fluidised bed temperature in the range 500 to 1100°C as shown in Figure 9. Figure 10 indicates however that the bed efficiency was greater at the lower temperatures.

The alumina coating rate at a fluidised bed temperature of 1000°C is shown as a function of the reactant feedrates in Figure 11. The coating rate is apparently a linear function of the aluminium chloride feedrate for $\text{AlCl}_3/\text{H}_2\text{O}$ feedrate ratios less than about 0.6. At higher ratios, for water vapour feedrates of 0.033 to 0.06 g/min., the coating rate appears to pass through a maximum and then decrease with further increases in aluminium chloride feedrate.

Scatter in the experimental points is attributed to variations within the range of water vapour feedrates

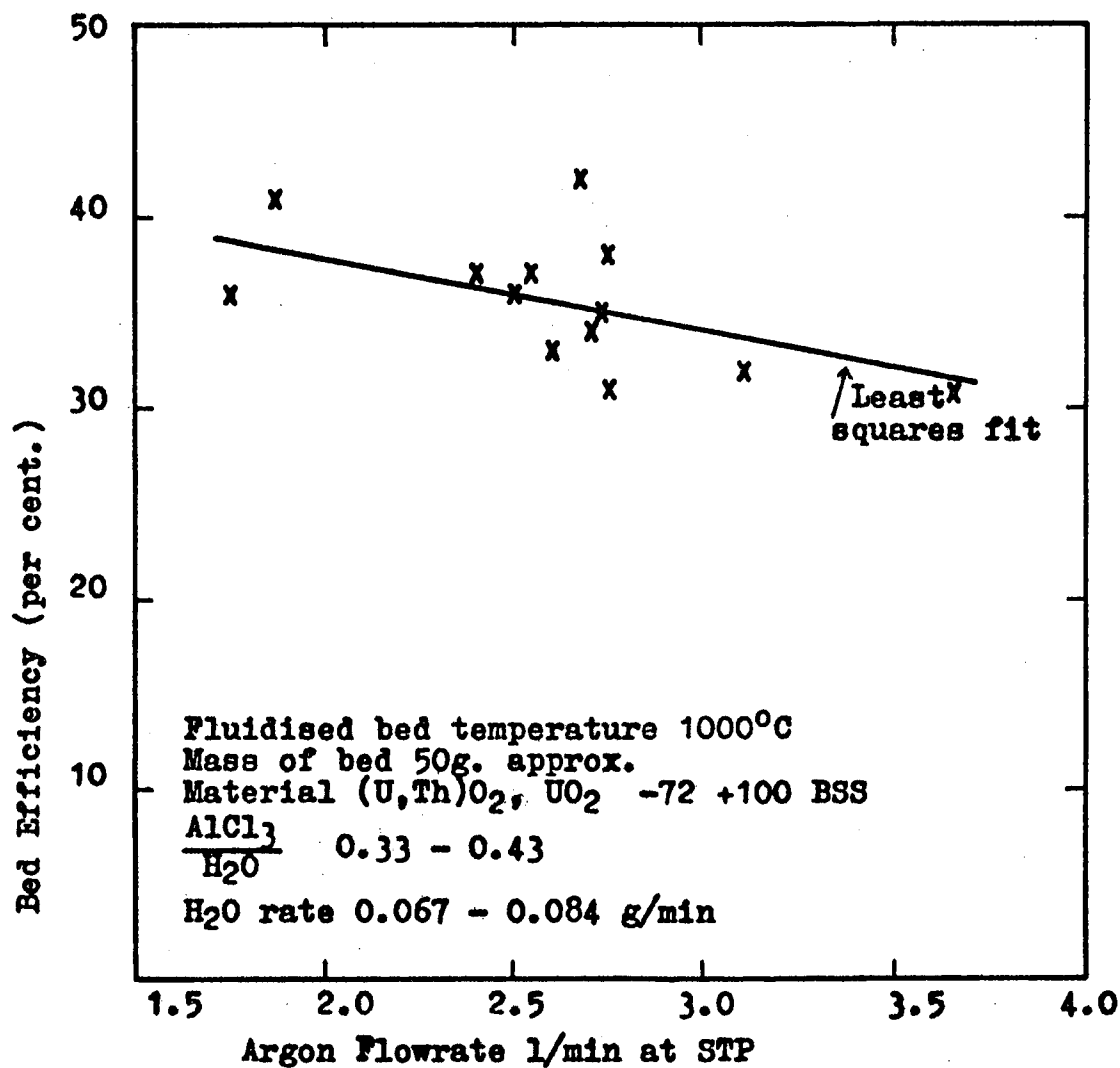


FIGURE 7 EFFECT OF FLUIDISING GAS FLOWRATE ON THE BED EFFICIENCY

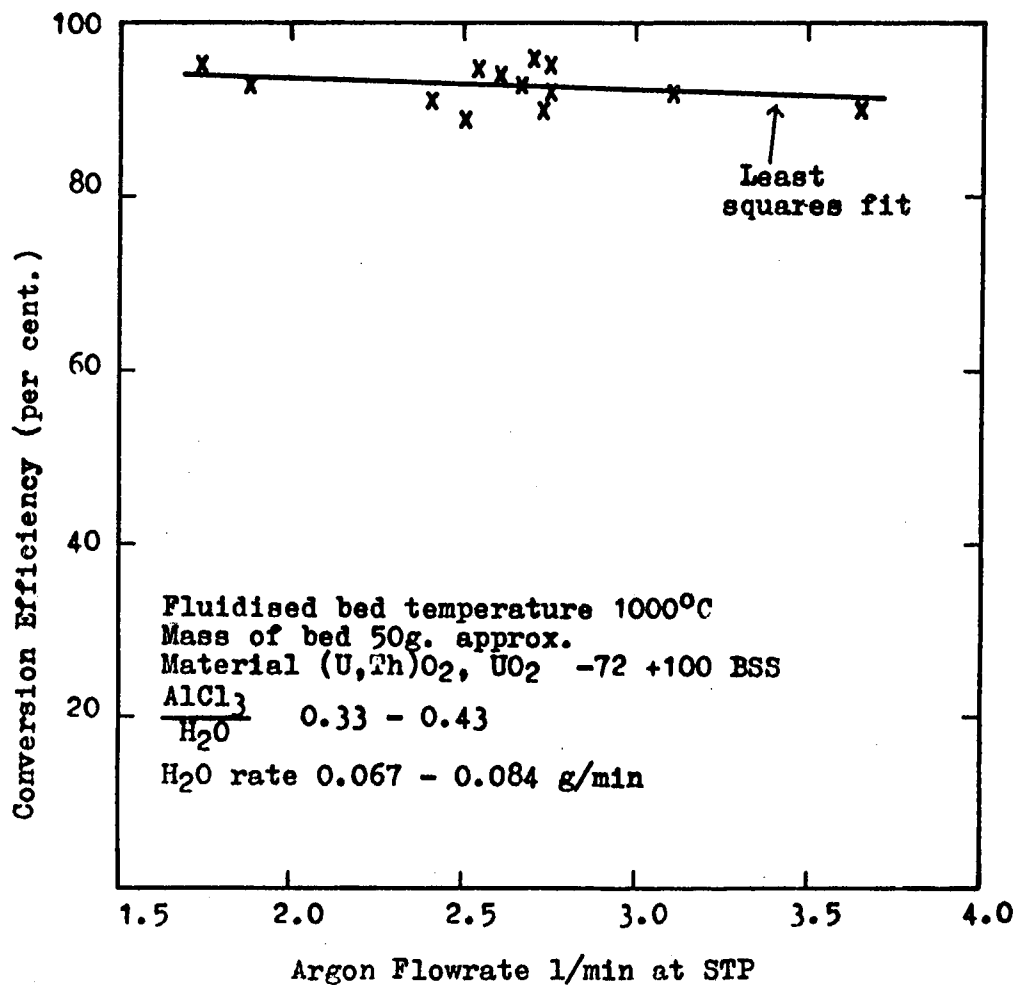


FIGURE 8 EFFECT OF FLUIDISING GAS FLOWRATE ON THE CONVERSION EFFICIENCY
 OF THE ALUMINIUM CHLORIDE HYDROLYSIS REACTION

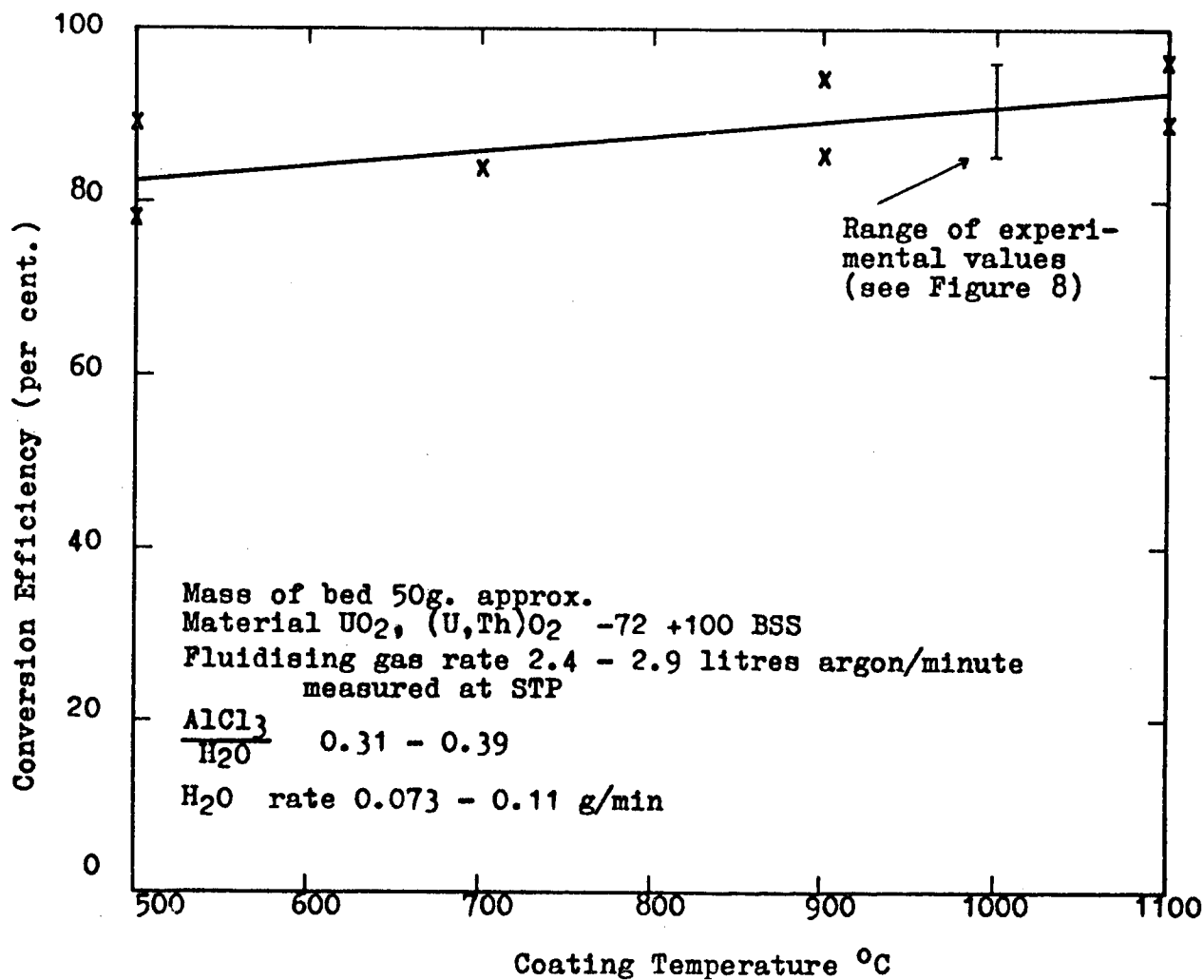


FIGURE 9 EFFECT OF TEMPERATURE ON THE CONVERSION EFFICIENCY
 OF THE ALUMINIUM CHLORIDE HYDROLYSIS REACTION

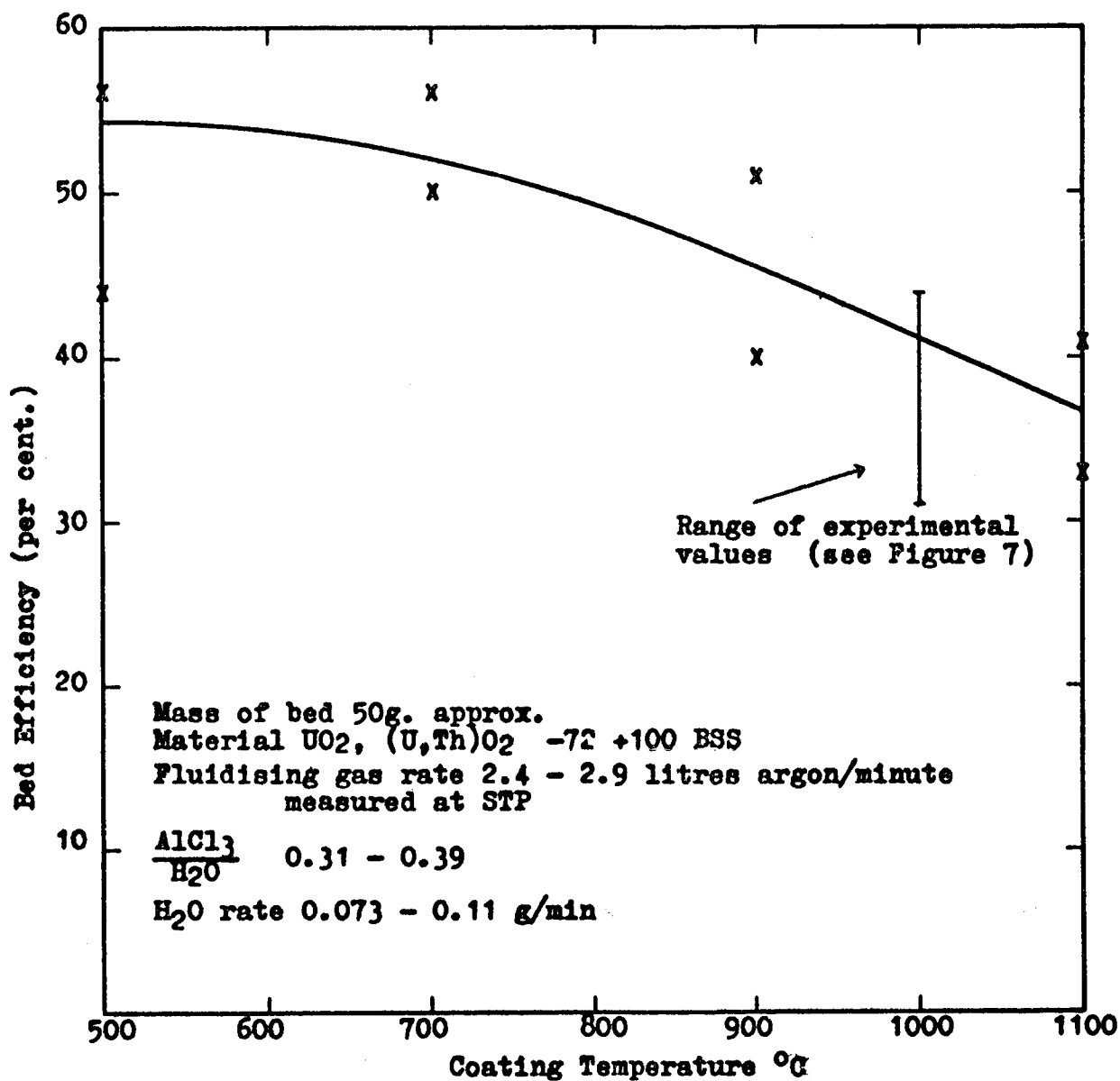


FIGURE 10 EFFECT OF TEMPERATURE ON BED EFFICIENCY

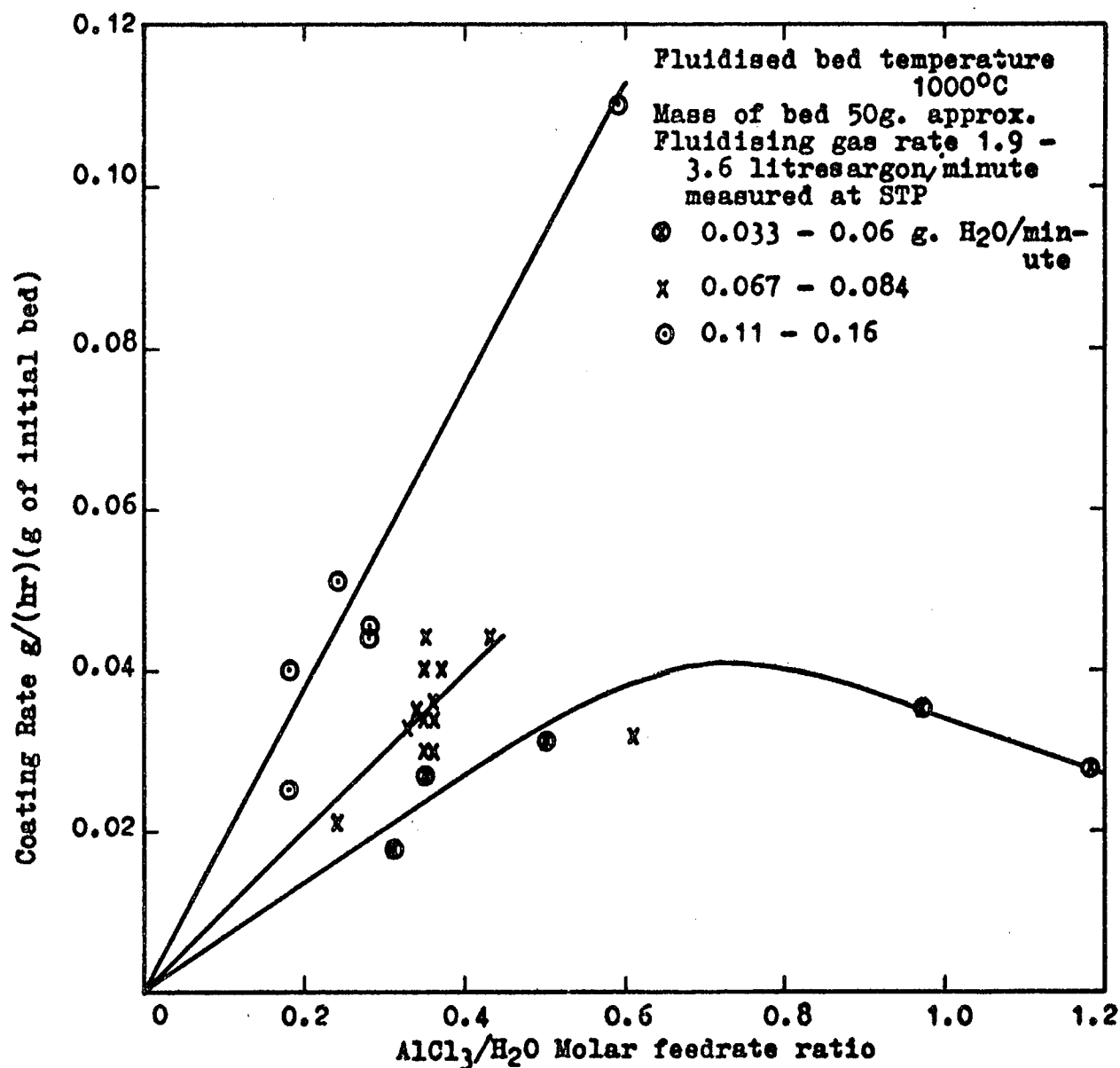
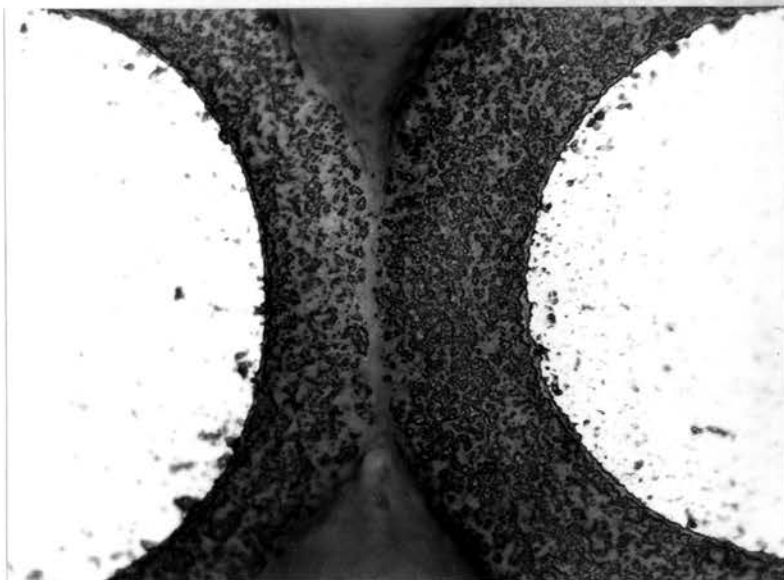


FIGURE 11 ALUMINA COATING RATES AT 1000°C

represented by each line of these figures, random errors in measurement, and variations in the quality of fluidisation in the various runs. The latter is attributed to variations in the fluidising gas velocity and to the difficulty of reproducing the bed geometry when new fluidised bed apparatus was fabricated due to breakages. In particular, the central position of the gas inlet tube and the 2 mm restriction at the bottom of the bed were difficult to maintain accurately.

5.2.2 Structure

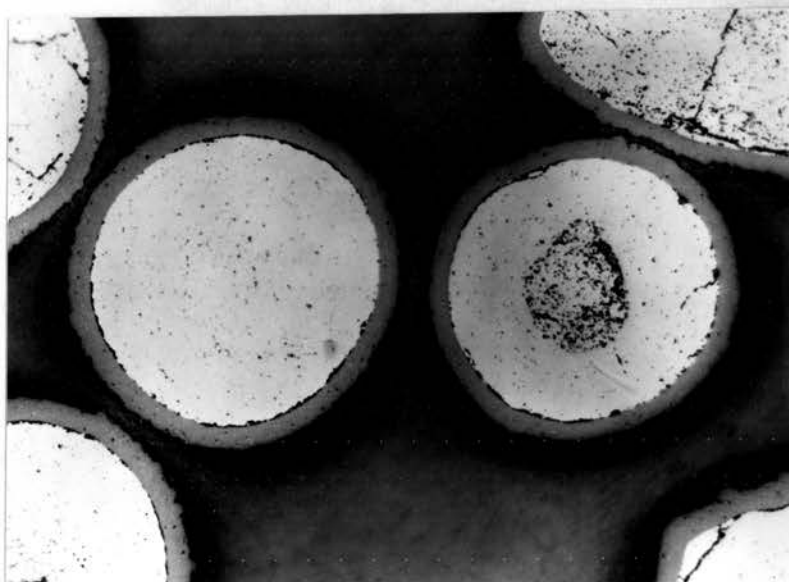
Coatings deposited at a fluidised bed temperature of 500 to 900°C were porous (Figure 12) with mean values of Knoop hardness (measured with a 25 gram load) in the range 90-700 kg/mm². At a fluidised bed temperature of 1000°C, the coatings produced were generally relatively dense and translucent (Figure 13) with Knoop hardnesses up to 3200 kg/mm². For coating rates of 1 to 3 microns per hour, coatings with the highest Knoop hardnesses were deposited with an AlCl₃/H₂O molar feedrate ratio of 0.35 to 0.38 (Figure 14). The Knoop hardnesses are shown as the mean $\pm$ standard deviation. For AlCl₃/H₂O ratios of 0.28 - 0.45, the Knoop hardnesses of the coatings produced decreased with increasing coating rate above 2 to 3 microns per hour (Figure 15). For an AlCl₃/H₂O ratio of 0.35 and a coating rate of 20 microns per hour, a coating with a mean Knoop hardness of 960 kg/mm² was obtained. Coatings deposited at 1100°C (Figure 16) were apparently similar in properties to 1000°C coatings.



X500

Figure 12 - Alumina Coated UO_2 Particles
(Run A35-I)

Coating Temperature	900°C
Coating Thickness	25 microns



X250

Figure 13 - Alumina Coated UO_2 Particles
(Run A44-I)

Coating Temperature	1000°C
Coating Thickness	12 microns

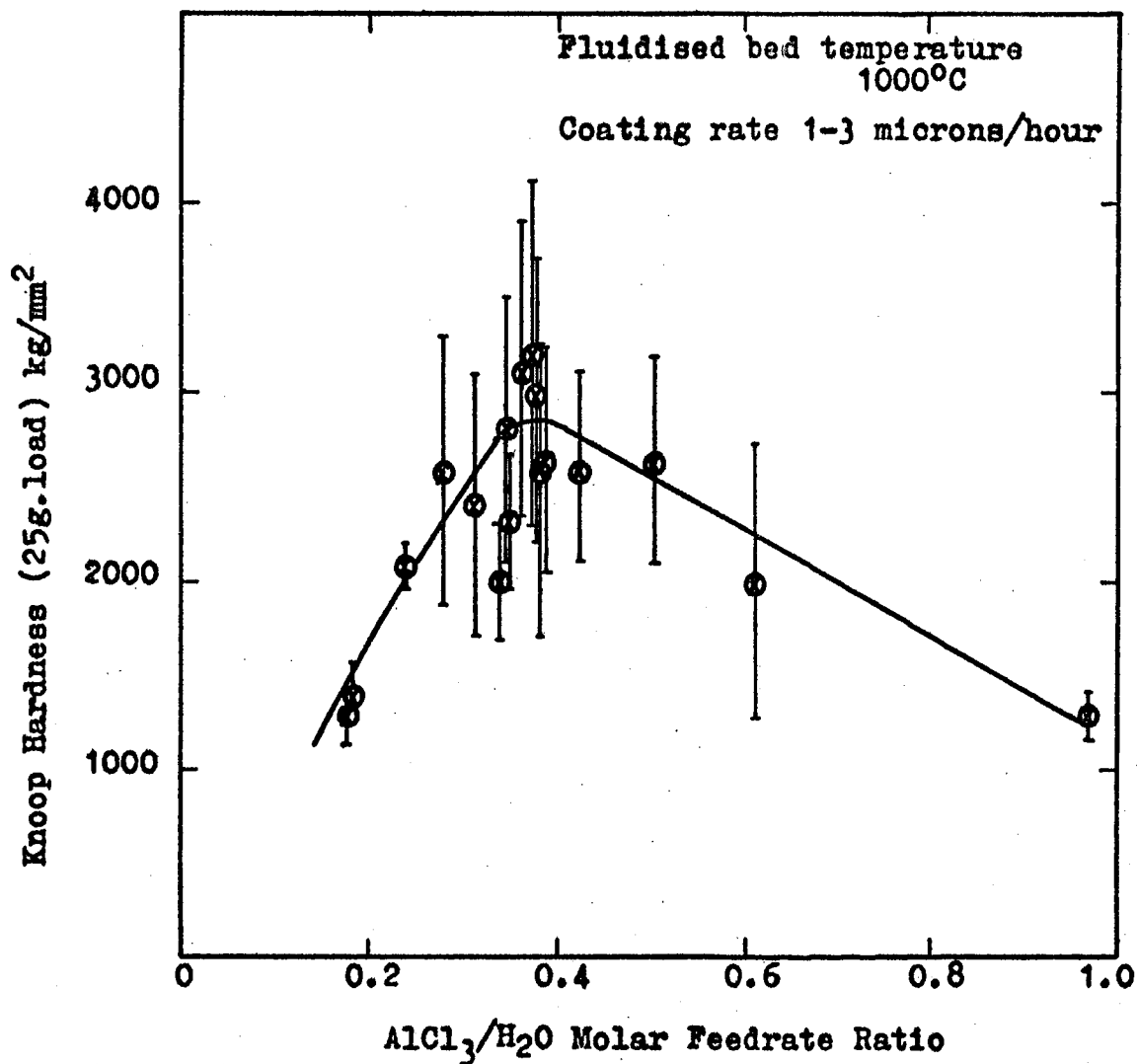


FIGURE 14 KNOOP HARDNESS OF ALUMINA COATINGS -
EFFECT OF REACTANT FEEDRATE RATIO

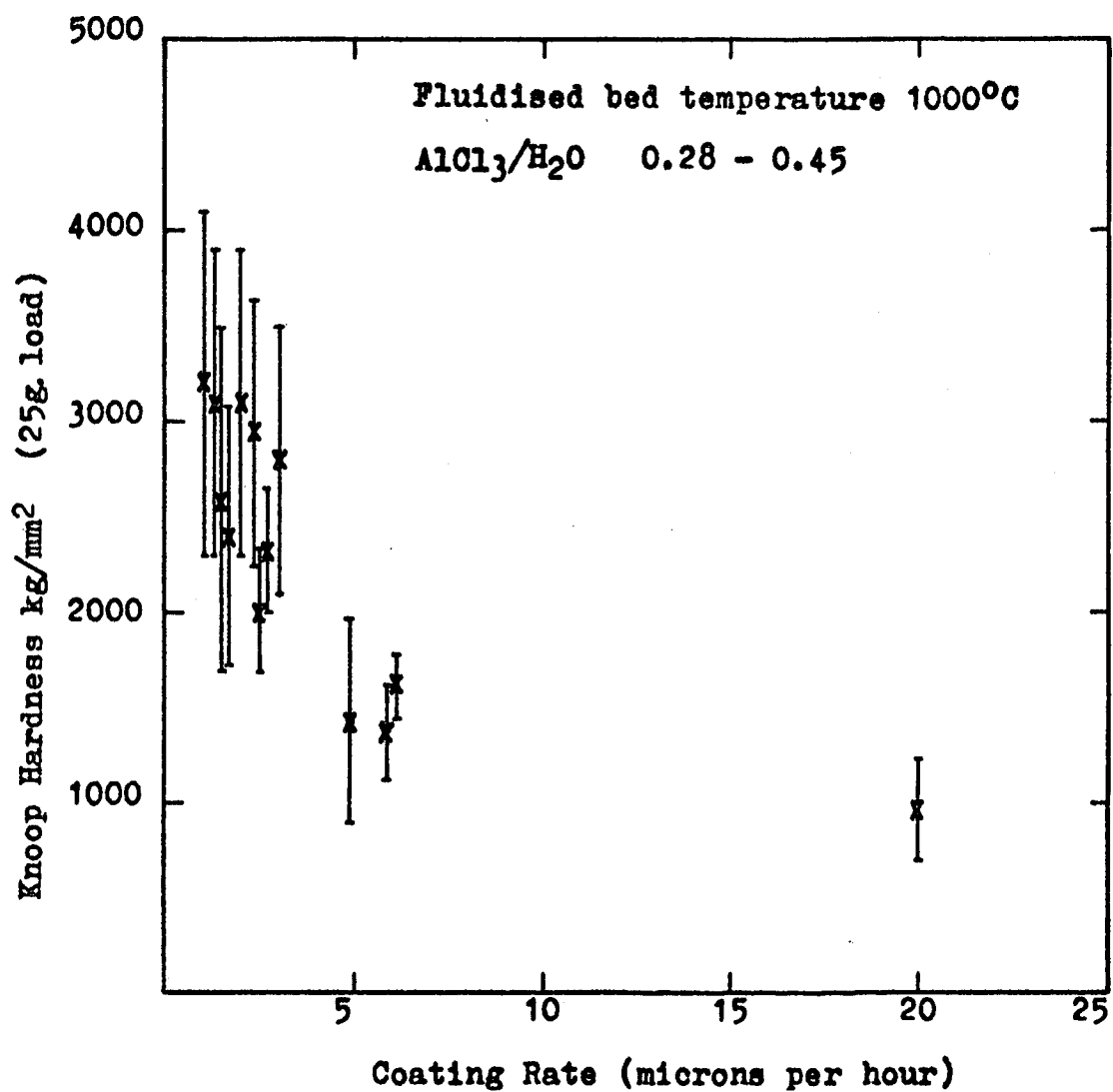
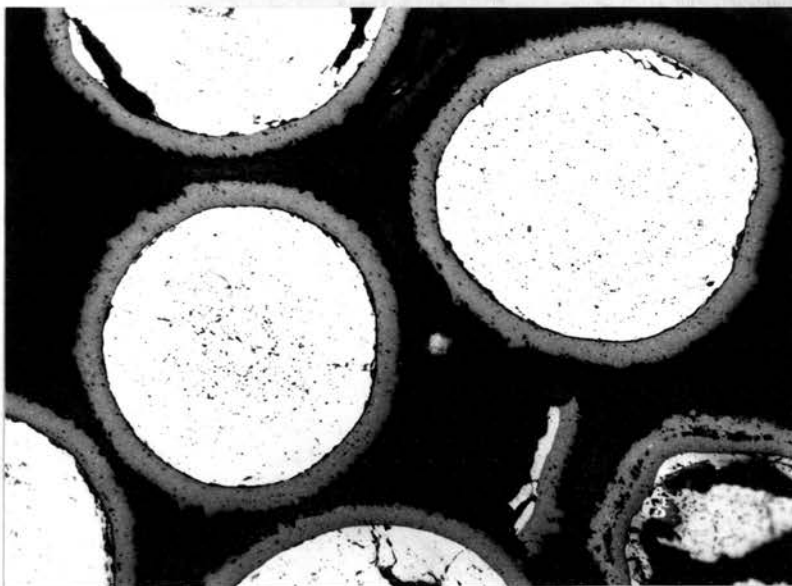


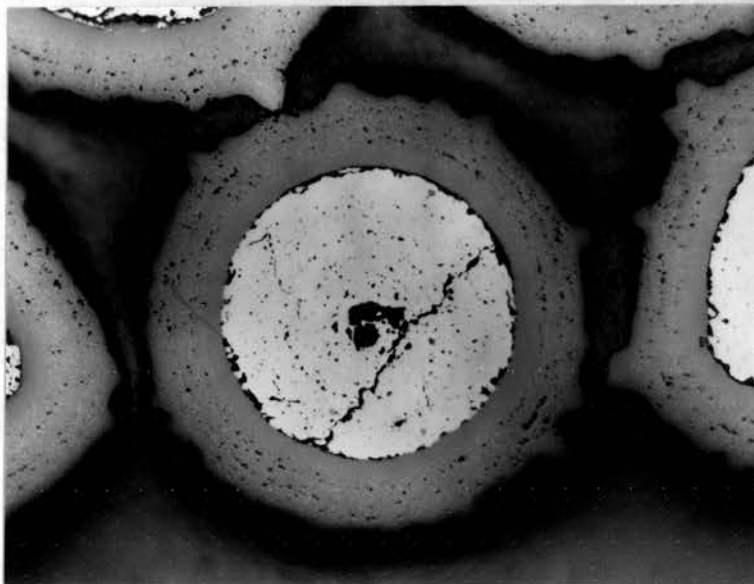
FIGURE 15 KNOOP HARDNESS OF ALUMINA COATINGS -
EFFECT OF COATING RATE



X250

Figure 16 - Alumina Coated UO_2 Particles
(Run A42-I)

Coating Temperature	1100°C
Coating Thickness	11 microns



X250

Figure 17 - Alumina Coated UO_2 Particles
(Run A43-VI)

Coating Temperature	1000°C
Coating Thickness	40 microns

There was some evidence of layering in coatings deposited at 1000°C and built up in a number of steps, as indicated by concentric rings of small pores (Figure 17). Penetration of the alumina into the substrate was also observed in some coatings deposited at 1000°C and 1100°C , suggesting the possibility of a core-coating reaction which produced a liquid phase at the coating temperature. In general, no marked surface protrusions were observed, although surface protruberances up to 25 microns long were detected on some coatings. The properties of coatings deposited, under similar reaction conditions, on UO_2 and $(\text{U,Th})\text{O}_2$ particles were not apparently influenced by the nature of the substrate. In alumina coatings deposited on UO_2 particles in a number of steps, the coating layer adjacent to the substrate appeared to be more dense than the outer layers, but no variation in Knoop hardness was observed.

X-ray diffraction analysis of coatings deposited in the range 750 to 1100°C revealed a finely crystalline alpha-phase alumina structure. There was some evidence of a glassy amorphous phase in coatings deposited at about 1000°C ; this agrees with results on alumina coatings deposited at 1000°C and reported by Dayton and Tipton (34). Examination of a coating deposited at 500°C showed an apparent lack of crystallinity, suggesting that the crystallite size was less than the detectable limit for this technique, that is, probably less than 0.05 microns.

5.2.3 Acid-Leach Tests

Acid-leach testing of alumina coated $(U,Th)O_2$ particles with nitric acid was unsatisfactory owing to variable thorium dissolution, since a catalysing ion such as fluoride ion is needed in the nitric acid to dissolve thorium. In a system where no such catalysing ions are present except those due to random impurities, dissolution of the thorium can be expected to be variable. These coated particles were also leached with 7.5 M nitric acid containing 0.005 M sodium fluoride to blanket the effect of random impurities and enhance thorium dissolution, and the results are compared in Table 4 with those obtained previously. Under these conditions consistent thorium dissolution results were obtained, but significant corrosion of the coating also occurred, giving a false impression of coating porosity.

Leaching of alumina coated UO_2 particles was shown to depend on the agitation conditions during leaching. Acid leaching with agitation was carried out in vertically mounted sealed capsules rotating about a horizontal axis at 9 rpm. The observed differences in the leaching results with and without agitation were shown to be significant statistically (Table 8).

TABLE 8EFFECT OF AGITATION IN ACID-LEACH TESTING

Run	Leaching without agitation		Leaching with agitation		Significance of observed difference in results
	No. in sample	U dissolved %	No. in sample	U dissolved %	
A19-I 0-6hrs	4	0.25 $\pm$ 0.02	4	0.40 $\pm$ 0.10	3% level
A23-IV 0-6hrs	4	0.016 $\pm$ 0.005	9	0.023 $\pm$ 0.011	25% level
A23-IV 6-12hrs	4	0.006 $\pm$ 0.0005	5	0.0029 $\pm$ 0.0015	3% level

These results suggest that diffusion of the acid through the coating is not the controlling step in the leaching process, and if it is assumed that the coatings are impermeable, then in the acid-leach test, uranium dioxide exposed as partly coated particles or surface contamination is probably being dissolved. In the case of porous coatings, the coating substrate is also dissolved.

Acid-leach testing of UO_2 particles coated with alumina at a fluidised bed temperature of 1000°C indicated that coatings deposited with an $\text{AlCl}_3/\text{H}_2\text{O}$ molar feedrate ratio of approximately 0.36 and a coating rate of 2 to 3 microns per hour gave most protection to the UO_2 substrate. For such a coating 12 microns in thickness (Run B19-I), 0.1 per cent of the contained urania

and 0.08 per cent of the alumina coating were dissolved in the second 6-hour leach.

For a coating built up to 40 microns in thickness in six steps under these conditions with an acid cleaning stage after each step to minimise urania surface contamination (Run A43-VI), 0.016 per cent of the contained urania was removed in the initial 6-hour leach, 0.0014 per cent in a second 6-hour period, and 0.00055 per cent in a third 6-hour period. Acid leach testing of a coating built up to 40 microns in thickness in 4 steps under the same conditions without intermediate cleanup (Run A23-IV), removed 0.023 per cent of the contained urania in the first 6-hour leach and 0.0029 per cent in the second 6-hour period. These data indicate the effectiveness of acid cleanup steps in reducing uranium contamination in the coatings. The particles were weighed before and after heating at 1000°C in air for one hour and no significant oxidation of the contained UO_2 was detected; subsequent acid leach testing confirmed that no coatings were ruptured in this test.

Acid leaching of fuel particles coated with alumina at temperatures in the range 500 to 1100°C dissolved varying amounts of the coating material (see Tables 3 and 4). These results indicate the effect of coating temperature on the nature of the coatings produced, in particular the porosity of coatings deposited at temperatures below 900°C .

5.2.4 Coating Contamination

Fuel contamination measured in alumina coated particles varied from 0.002 to 0.6 per cent of the contained substrate. In coatings built up in a number of steps to about 40 microns in thickness (Runs A23-IV and A43-VI), intermediate acid-cleanup (Run A43-VI) reduced the uranium contamination to acceptable levels, as determined by acid-leach testing and measurement of alpha-particle emission.

Silicon and residual chloride ion concentrations in the alumina coatings were in the ranges 300 to 1400 ppm and 240 to 12,400 ppm respectively. These impurity contents could not be correlated with operating variables such as coating temperature or reactant feedrate ratio, nor could coating properties be related to them in any way.

5.2.5 Fission Gas Release Measurements

UO₂ particles coated with 40 microns of alumina, deposited at 1000°C with an AlCl₃/H₂O molar feedrate ratio of approximately 0.36 and a coating rate of 2 to 3 microns per hour (Run A23-IV), were evaluated by neutron activation and post irradiation annealing (7). A sample of the particles was irradiated in a thermal neutron flux of 1 to 2 x 10¹³ nv for 65 hours at approximately 100°C. Xenon-133 release was measured for successive post irradiation annealing experiments in the range 900 to 1300°C. The cumulative fractions released are shown in Table 9.

TABLE 9XENON-133 RELEASE FROM ALUMINA COATEDUO₂ PARTICLES

Sample	Annealing Temperature °C	Annealing Time	Cumulative Fraction Xe-133 Released
1	900	5.5 hours	6.9×10^{-4}
	1000	4	2.8×10^{-3}
	1100	5	4.7×10^{-3}
2	1000	3	1.9×10^{-3}
	1100	18	5.0×10^{-3}
	1200	5.5	1.1×10^{-2}
	1300	2	1.4×10^{-2}

At 900°C and 1000°C an initial burst of gas was observed followed by a slow diffusion-controlled release. This initial release may have been due to imperfections in some of the coatings, though this is unlikely on the basis of the initial evaluation tests, or to surface contamination of the coatings. At 1100°C similar behaviour was observed initially and thereafter irregular bursts of gas occurred, probably associated with failure of individual particle coatings. This explanation is supported by the observed increase in the size and frequency of the bursts of fission gas at 1200°C and 1300°C. Tensile stresses in the coating due to the difference in thermal expansion of urania and alumina were possibly responsible for coating failure at annealing temperatures above the coating deposition temperature of 1000°C.

5.3 Results of Beryllia Coating Studies

5.3.1 Conditions of Deposition

Most of the beryllia coating runs were made at 1000°C to produce coatings up to 40 microns in thickness at coating rates of 1 to 8 microns per hour, under conditions similar to those used in the alumina coating runs. Some preliminary coating runs were made at a coating temperature of 1400°C.

Beryllium chloride prepared by the chlorination of beryllium metal turnings and also material obtained from Brush Beryllium Co. showed no apparent differences in performance in beryllia coating studies. Details of semi-quantitative spectrographic analyses of samples of the two materials are given in Table 10 for comparison. The presence of much greater amounts of copper, chromium and nickel in the beryllium chloride produced by the chlorination of beryllium turnings is attributed to corrosion of the metering equipment, and gas lines leading to the apparatus, by the chlorine.

The conversion efficiency of the beryllium chloride hydrolysis reaction at 1000°C is shown in Figure 18. For a constant water vapour feedrate, the efficiency falls with increasing values of the $\text{BeCl}_2/\text{H}_2\text{O}$ molar feedrate ratio. Within the range of the variables studied and the accuracy of the available data, increasing the water vapour feedrate apparently has no effect on the conversion efficiency.

Usually 30 to 40 per cent of the beryllia fed to the reactor as beryllium chloride was deposited as coating on the

TABLE 10
SPECTROGRAPHIC ANALYSIS OF BERYLLIUM CHLORIDE

Element	Order of Concentration ppm	
	Brush Beryllium Co.	Chlorination of Be Turnings
Mg	500	500
Ca	100	500
Al	500	20
Si	500	500 - 2000
Cu	20	500
Fe	500	500
Cr	Not detected	100
Ni	Not detected	500 - 2000

Li, Na, K, Cs, Sr, Ba, Sn, Pb, P, As, Sb, Bi, Ag, Au, Zn, Cd, Hg, Ti, Zr, V, Mo, W, Mn, Co, B, Nb, In, Th, Ta were not detected.

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particles, for $\text{BeCl}_2/\text{H}_2\text{O}$ feedrate ratios less than 0.8. Variation in particle size and hence surface area in runs where coatings were built up in a number of steps to about 50 microns in thickness had no significant effect on the efficiency of the fluidised bed. At higher values of the feedrate ratio, less than 20 percent of the oxide was deposited as coating on the particles.

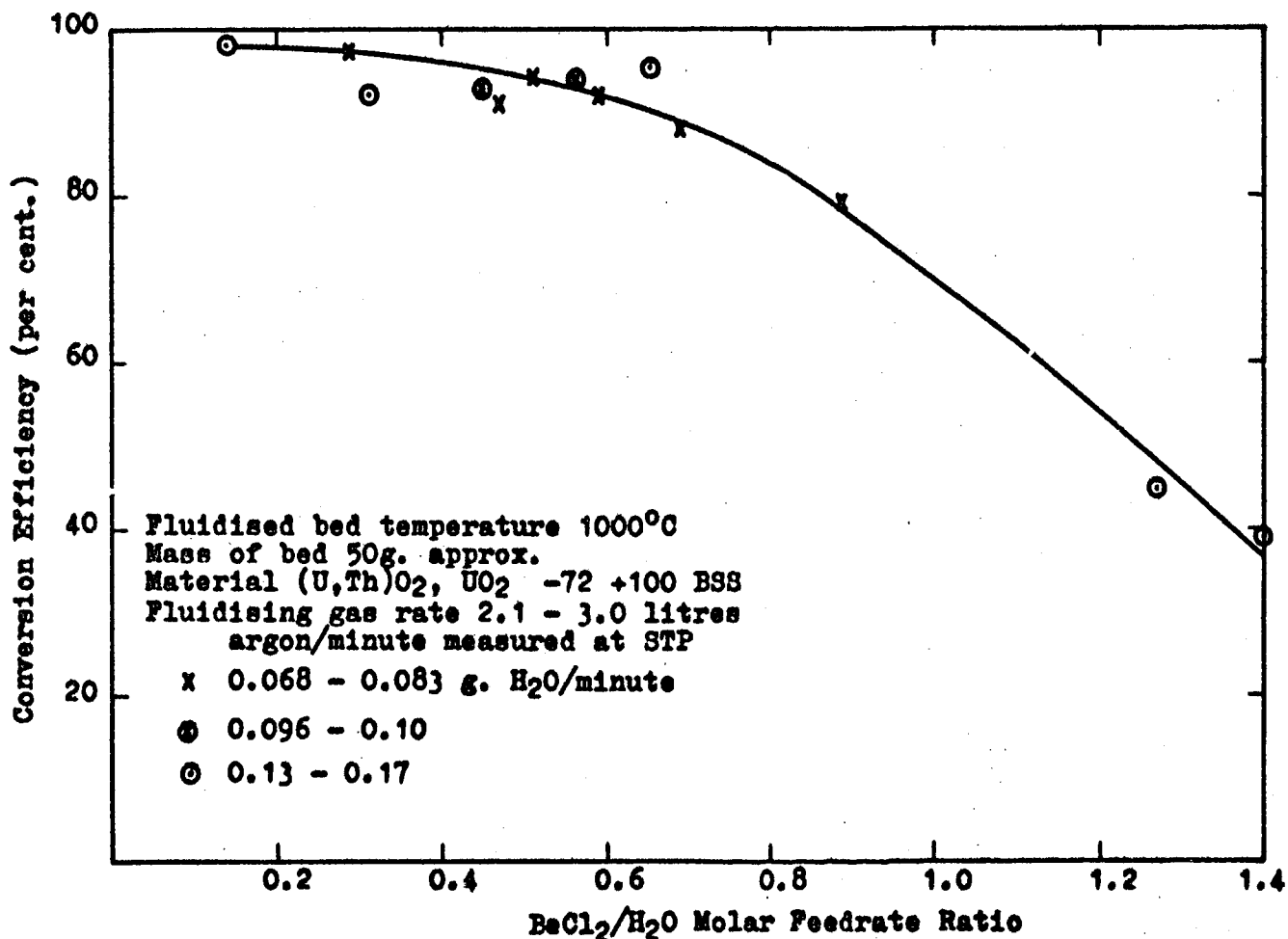


FIGURE 18 CONVERSION EFFICIENCY OF THE BERYLLIUM CHLORIDE HYDROLYSIS REACTION

The beryllia coating rate is shown as a function of the reactant feedrates in Figure 19. The beryllia coating rate is a linear function of the beryllium chloride feedrate for $\text{BeCl}_2/\text{H}_2\text{O}$ ratios less than 0.7 within the limits and accuracy of the experimental data. Scatter in the experimental points is attributed to the same factors outlined for the alumina coating data.

5.3.2 Structure

Metallographic examination of beryllia coatings deposited at 1000°C indicated that in all cases surface protrusions had formed on the coatings (Figure 20). The protrusions became more prominent as the coating thickness increased. All coatings were microcrystalline and apparently porous on the fine scale. Coatings were most dense near the particle-coating interface and along the spine of the spikes, and more porous in the regions formed by adjoining protrusions (Figure 21). No evidence of layering was observed in coatings built up in a number of steps and there was good cohesion between the coatings and the substrate.

The variation in Knoop hardness of the coatings with molar feedrate ratio of the reactants $\text{BeCl}_2/\text{H}_2\text{O}$ is shown in Figure 22, for coating rates in the range 1.3 to 3.5 microns per hour. The Knoop hardnesses are shown as the mean $\pm$

Fluidised bed temperature 1000°C

Mass of bed 50g. approx.

Material (U,Th)O₂, UO₂ -72 +100 BSS

Fluidising gas rate 2.1 - 3.0 litres argon/minute measured at STP

x 0.068 - 0.083 g H₂O/minute

⊙ 0.13 - 0.17

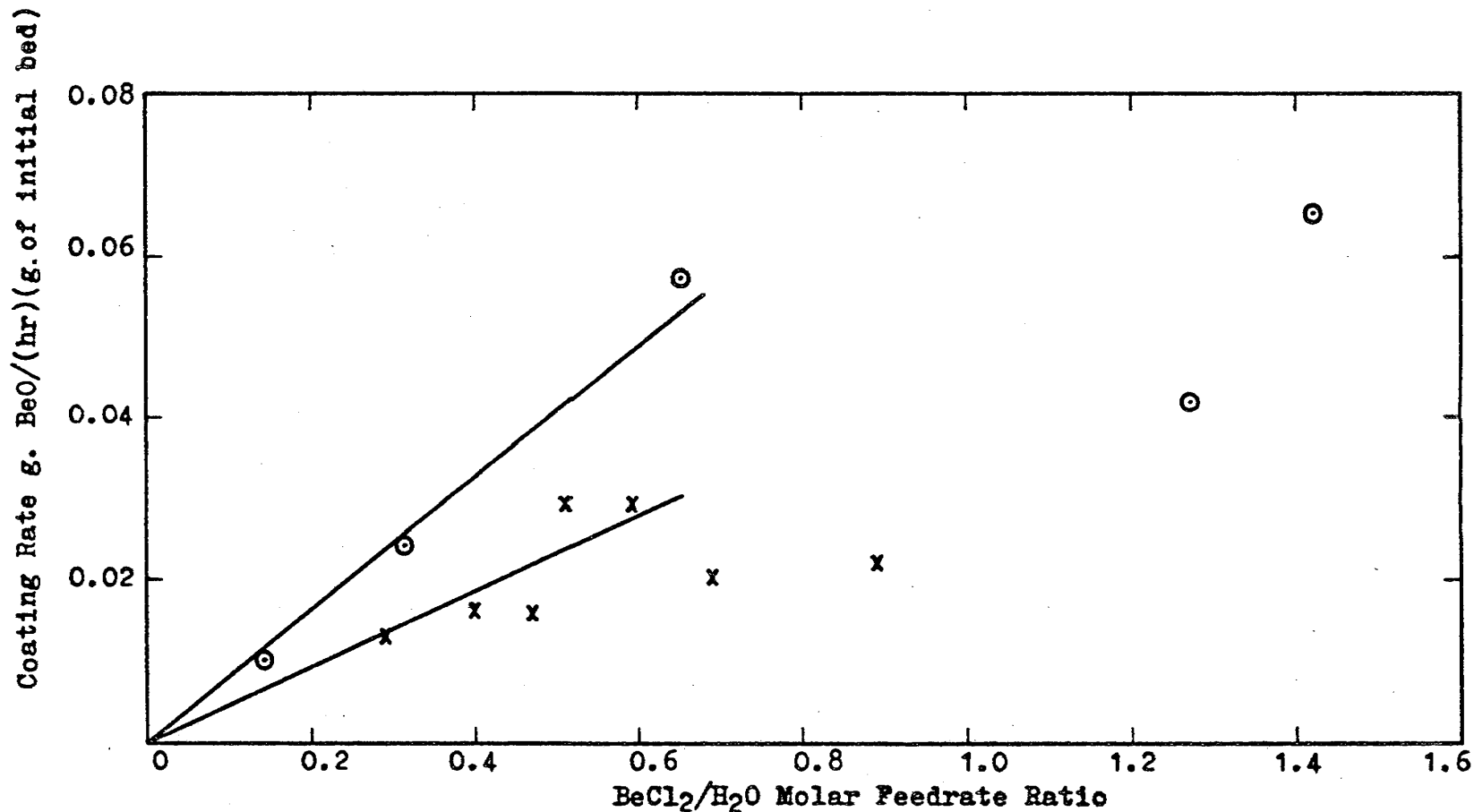
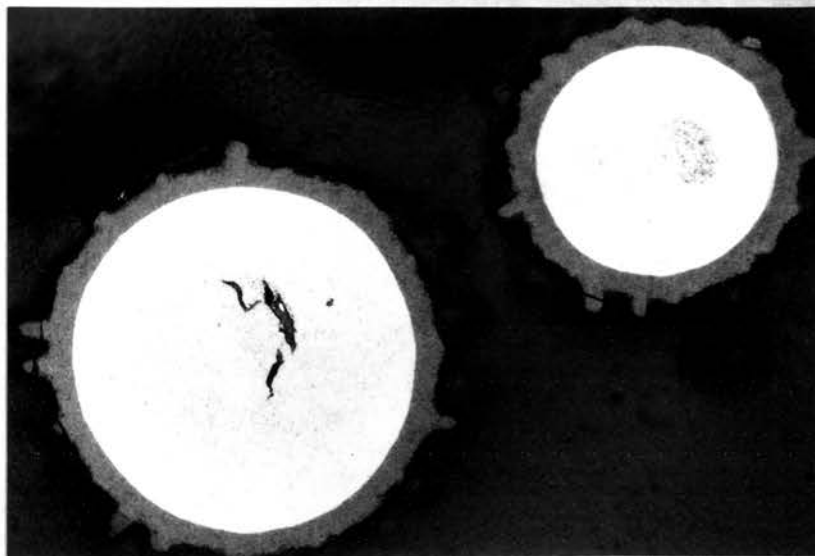


FIGURE 19 BERYLLIA COATING RATES AT 1000°C



X250

Figure 20 - Beryllia Coated UO_2 Particles
(Run B14-I)

Coating Temperature	1000°C
Coating Thickness	15 microns



X250

Figure 21 - Beryllia Coated UO_2 Particles
(Run B14-IV)

Coating Temperature	1000°C
Coating Thickness	40 microns

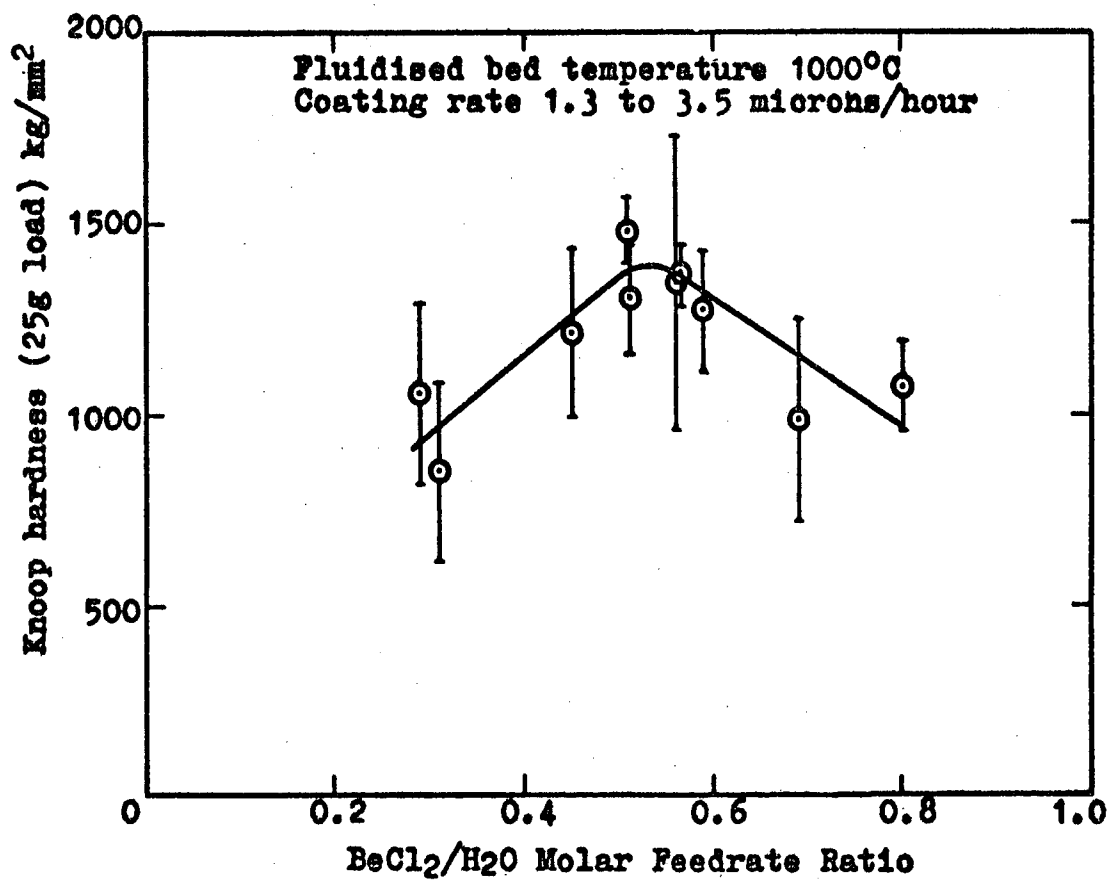


FIGURE 22 KNOOP HARDNESS OF BERYLLIA COATINGS -
EFFECT OF REACTANT FEEDRATE RATIO

standard deviation. A $\text{BeCl}_2/\text{H}_2\text{O}$ ratio of approximately 0.5 appears to give the hardest coating for a maximum coating rate of about 3 microns per hour. At higher coating rates and other reactant ratios, more porous coatings were produced.

Initial beryllia coating runs at 1400°C failed to produce a uniform coating. The coatings deposited consisted of a thin, coherent, dense layer of beryllia on the UO_2 surface and well developed columnar grains of beryllia up to 40 microns long attached to this layer with their c-axis generally normal to the UO_2 surface. Later runs produced coatings which were relatively dense and consisted of a layer of granular beryllium oxide generally one to two grains thick (Figure 23). Most of the grains were less than 10 microns in diameter. The average Knoop hardness of the coatings was in the range 1100 to 1200 kg/mm^2 .

5.3.3 Permeability Tests

Acid-leach and air oxidation tests of the beryllia coated UO_2 particles indicated that coatings deposited at 1000°C did not give satisfactory protection of the urania under these conditions. Up to 75 per cent of the contained UO_2 was oxidised by heating the particles at 1000°C in air for one hour, as determined by weighing the sample before and after this test. Acid leaching of the coated particles with 7.5 M nitric acid for 6 hours at 90°C under agitated

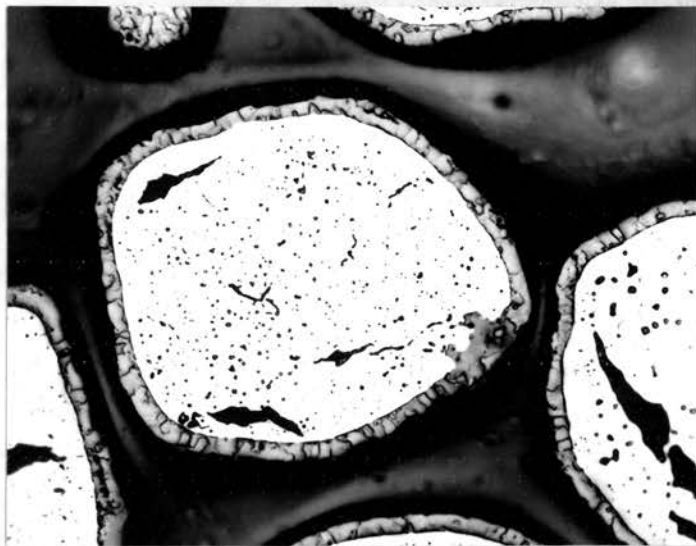


Figure 23 - Beryllia Coated $(U,Th)O_2$ Particles
(Run B19-I)

Coating Temperature 1400 °C
Coating Thickness 8 microns

conditions dissolved as much as 80 per cent of the beryllia coating as well as up to 96 per cent of the contained urania. Least beryllia was dissolved from coatings deposited with a $\text{BeCl}_2/\text{H}_2\text{O}$ molar feedrate ratio of 0.5 to 0.6. Evaluation of a coating of this type, built up to 40 microns in thickness (Run B14-IV), indicated that 50 per cent of the contained urania was oxidised in the standard air oxidation test and that 25 per cent of the beryllia coating and 40 per cent of the contained urania were removed in the first 6 hours of the standard acid-leach test. These data indicated the porous nature of coatings deposited at a fluidised bed temperature of 1000°C .

The only coating deposited at 1000°C which showed merit on the basis of these tests was subsequently found to contain 16 per cent silicon contamination (Run B5-I) and therefore was not considered for further evaluation at this stage, since such impurities would complicate irradiation studies. UO_2 particles coated with beryllia at 1400°C (Run B18-I) also gave promising results in acid-leach tests.

5.3.4 Coating Contamination

Measurement of the alpha particle emission from the beryllia coated particles indicated uranium contamination in all coatings of the order of 0.05 to 1.0 per cent of the contained uranium. Silicon contamination in the coatings was generally in the range 2000 to 8000 ppm, although coatings

deposited in Run B5-I contained 16 per cent silicon. This coating showed improved performance over other beryllia coatings deposited at 1000°C, as indicated in Table 6, but no other relationship between coating conditions or coating properties and impurity levels was observed. Residual chloride ion concentrations in the coatings of up to 2900 ppm were determined.

5.3.5 Effect of Heat Treatment

Only small changes were observed in beryllia coated UO_2 particles (Run 14-IV) after heat treatment at 1500°C in nitrogen for two hours (Figure 24). Slight densification of the coating apparently occurred resulting in less porosity in the region of protrusions, and slightly greater Knoop hardness. Air oxidation testing indicated that the beryllia coating did not give adequate protection to the contained urania after heat treatment although it was slightly better than in the as-produced condition. Approximately 7 per cent of the UO_2 was oxidised after heat treatment compared with 50 per cent oxidised in the as-produced condition.

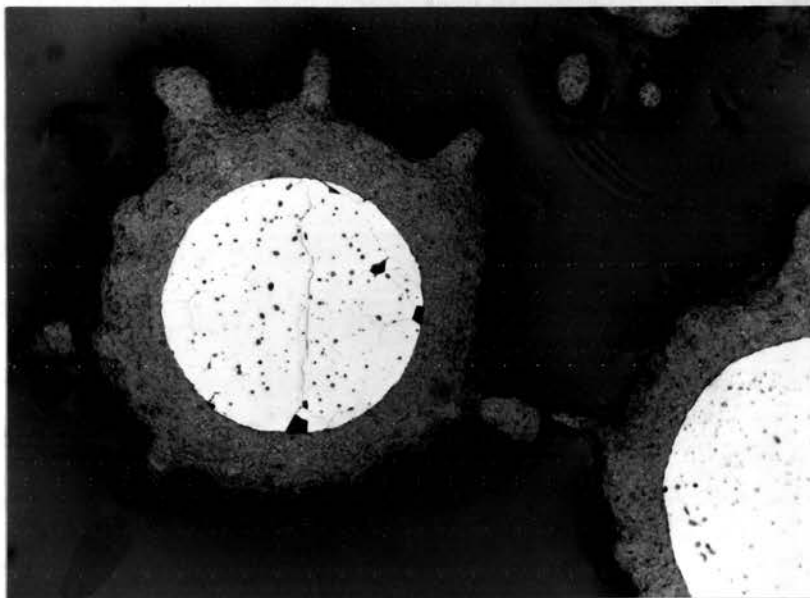


Figure 24 - Beryllia Coated UO_2 Particles
(Run B114-IV)

Coating Temperature 1000°C
Heat treated 1500°C in nitrogen
for 2 hours

CHAPTER 6

DISCUSSION OF RESULTS

6.1 Conditions of Deposition

6.1.1 Performance of the Fluidised Bed

A comparison of the per cent of oxide deposited as coating (the bed efficiency) and the percent of chloride hydrolysed in the fluidised bed reactor (the conversion efficiency) indicates that, within the accuracy of the experimental data, the ratio of these two quantities is apparently independent of the reactant feedrates (Figures 25, 26). In addition, this ratio was not influenced by variation in particle size in runs where coatings were built up in a number of steps, and only slightly affected by variation in the mass of the bed of particles, but it decreased with increasing fluidising gas flowrates (Figure 27). This suggests that, of the chloride hydrolysed in the reactor, the proportion which becomes coating on the particles depends on the solids-gas contact which is a function of the quality of fluidisation. For a given fluidised bed reaction system, the quality of fluidisation varies with the geometry of the bed and the fluidising gas velocity.

Similar results have been reported by Ciborowski and Wronski (54,55) for the condensation of naphthalene in a cooled fluidised bed. In their work, the efficiency of

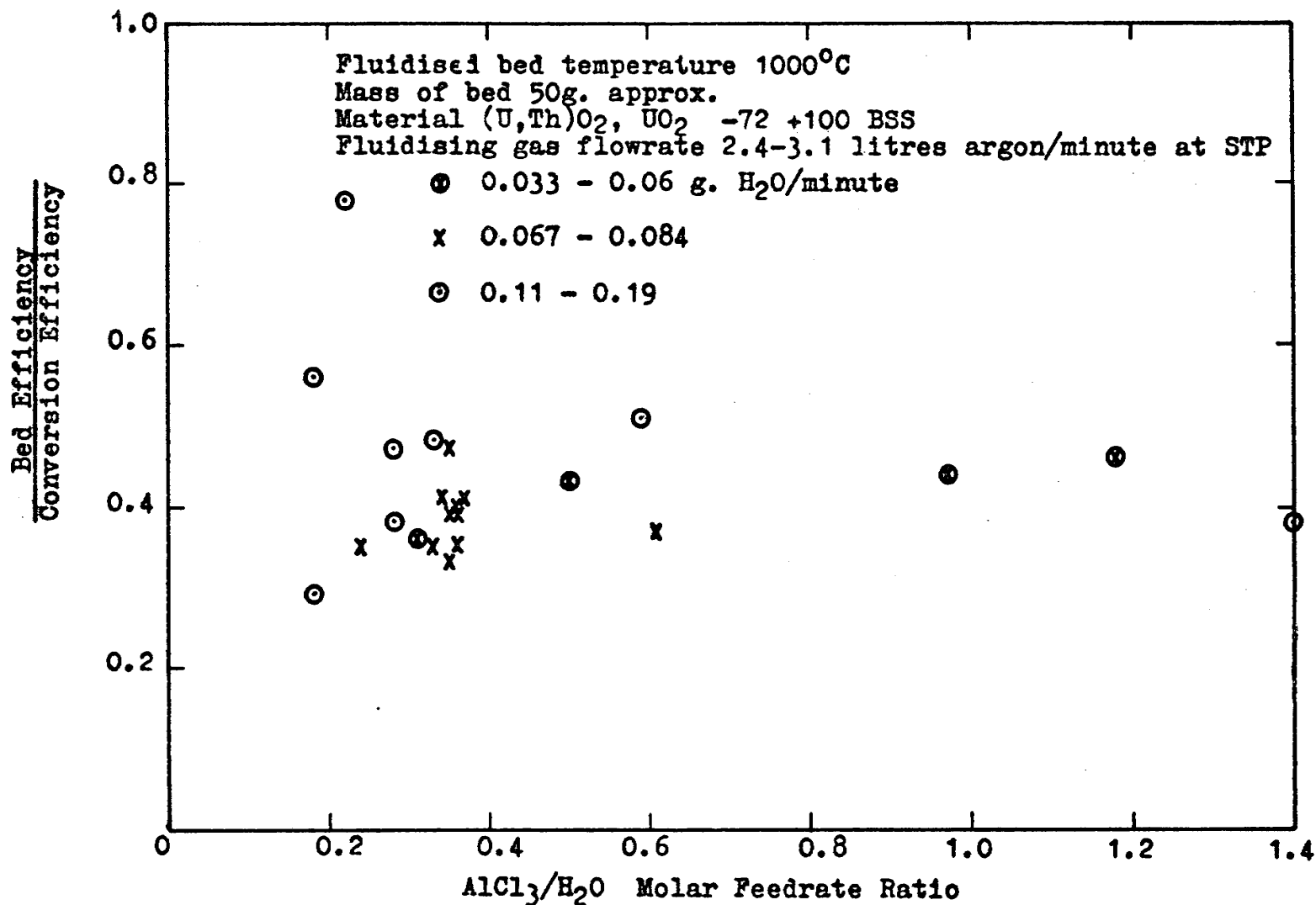


FIGURE 25 EFFECT OF REACTANT FEEDRATES ON BED EFFICIENCY CONVERSION EFFICIENCY FOR ALUMINA COATING DEPOSITION

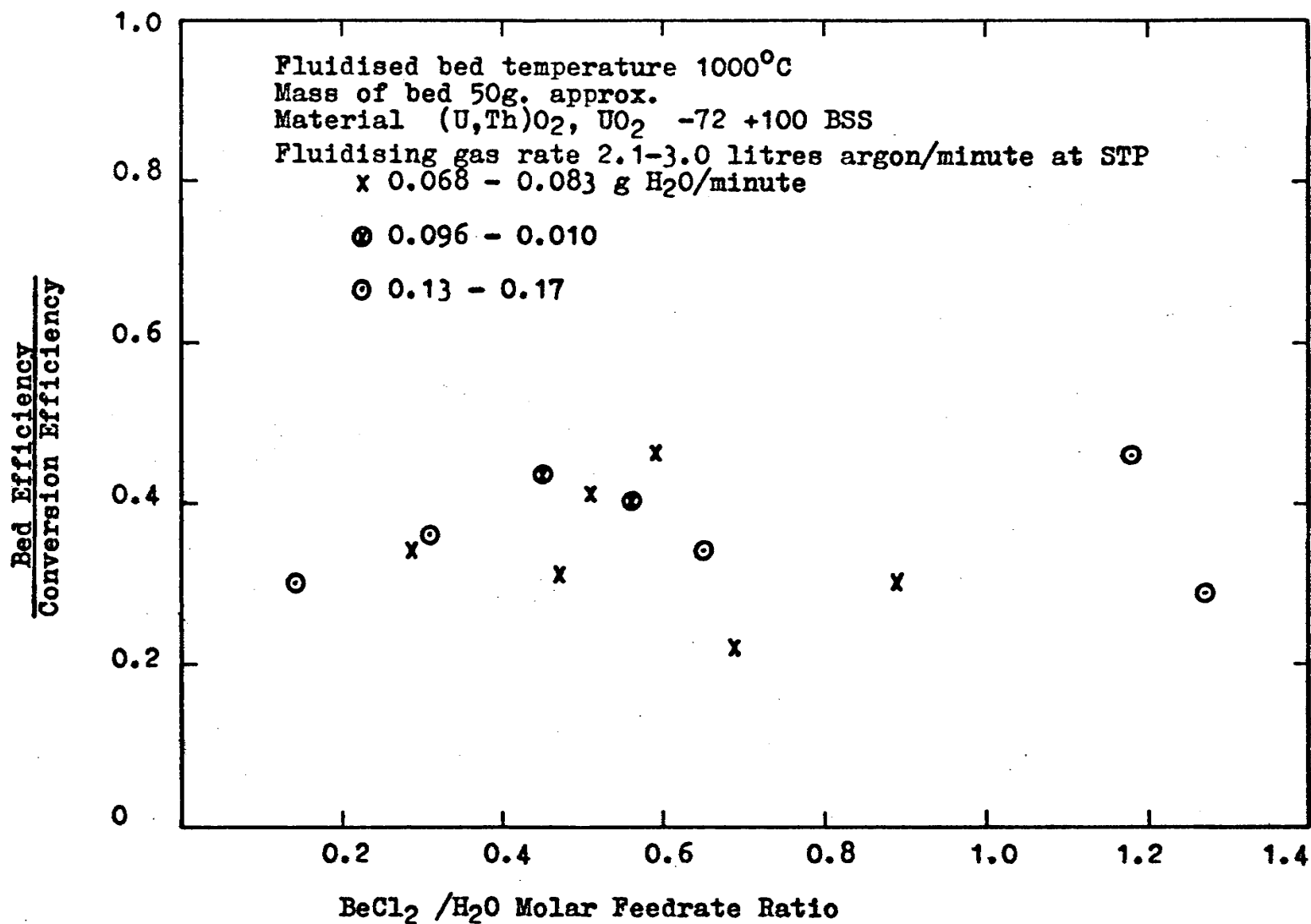


FIGURE 26 EFFECT OF REACTANT FEEDRATES ON BED EFFICIENCY / CONVERSION EFFICIENCY FOR BERYLLIA COATING DEPOSITION

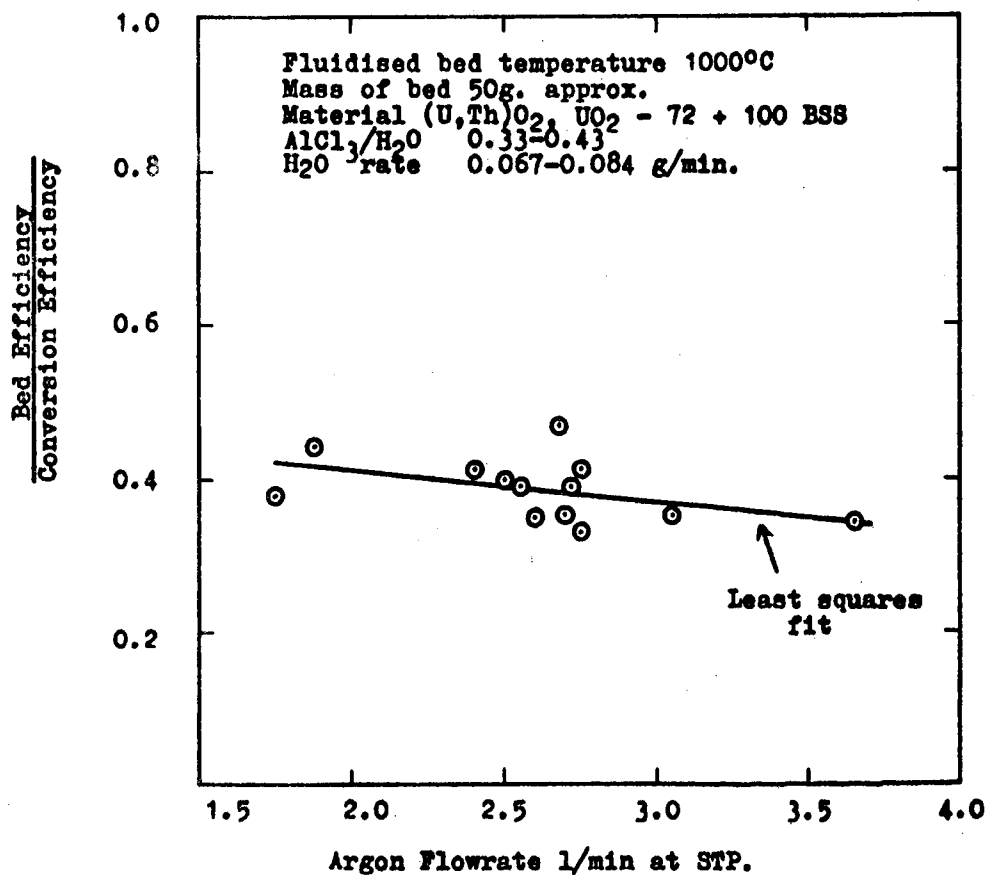


FIGURE 27 EFFECT OF FLUIDISING GAS FLOWRATE ON ~~BED EFFICIENCY~~
 FOR ALUMINA COATING DEPOSITION ~~CONVERSION EFFICIENCY~~

condensation, defined as the ratio of the amount of naphthalene crystallised in the bed to the total amount in the feed to the fluidised bed, varied from 70 to 100 per cent and was not influenced by the mass of the bed and the diameter of the particles in the bed, but decreased with increasing values of the fluidising gas velocity. These results indicated that, under the conditions of supersaturation in the bed, condensation of the naphthalene was not limited by the velocity of crystallisation. It was concluded that the yield of crystallisation on the particles was principally controlled by the process of self-nucleation of the sublimate in the gas phase. Ciborowski and Wronski proposed that the conditions of aggregative fluidisation observed in their work were favourable to self nucleation in the gas phase. An increase in the velocity of the gas flow caused an increase in the degree of heterogeneity of the bed, and this favoured self-nucleation in accordance with the results obtained concerning the dependence of the efficiency of condensation on the fluidising gas velocity.

Similar arguments could be advanced to explain the results obtained in this investigation. The flow of gas through a gas-solids fluidised bed occurs as gas bubbles rising through the bed with a wake of particles which travel with the bubble and give rise to solids mixing, and as interstitial gas flow remote from bubbles moving upwards

through the dense phase at approximately the minimum fluidisation velocity regardless of the overall flowrate through the bed (56). Observation of the behaviour of the fluidised bed in a perspex model at room temperature using argon as the fluidising gas indicated that the conical shape of the bed support and the single constriction at the bottom of the bed tended to promote bubble formation. A certain amount of violent bubble action is considered to be desirable to give uniform solids mixing in the bed, and to break up potential agglomerates of particles and prevent the formation of doublets, for example, by bridging during coating deposition.

For a given fluidised bed temperature, decreasing the fluidising gas rate reduces the volume of gas bubbles passing through the bed and a greater proportion of the reactant gases contact the particles to produce coating on the particles. Similarly for a given fluidising gas flowrate, reducing the fluidised bed temperature decreases the ratio of gas velocity to the minimum fluidising velocity ($G/G_{\min}$) and consequently changes the quality of fluidisation promoting less bubble formation. As a result, there is less tendency to gas phase nucleation and more of the oxide deposits as coating on the particles. Changing the reaction temperature may however influence factors other than the quality of fluidisation and care must be exercised in the interpretation

of such data. For example, a change in the reaction equilibrium at a lower temperature could give rise to an intermediate product which might have completely different nucleation characteristics to those of the reaction product obtained at a higher temperature.

6.1.2 Kinetics of the Hydrolysis Reactions

Correlation of the data obtained for the kinetics of the hydrolysis reactions is not possible because of the limited results available and the complexity of the reaction system. The conversion efficiencies obtained are integrated results over the fluidised bed reactor. Since the fluidised bed apparatus used was small in diameter (with a length to diameter ratio for the bed of 0.5 to 1.0), uniform solids mixing can be expected but little gas mixing would be achieved (57). On this basis the fluidised bed reactor probably corresponds more nearly to a plug-flow tubular reactor than to a perfectly mixed tank reactor. Thus computation of rate equations to describe the kinetics of the hydrolysis reactions is not justified on the basis of the existing data.

A qualitative comparison of the results obtained in this work with typical rate curves given by Yang and Hougen (58) for catalysed and uncatalysed gaseous reactions gives an indication of the types of reactions possibly involved in the coating of particles in a fluidised bed. Figure 28 is a

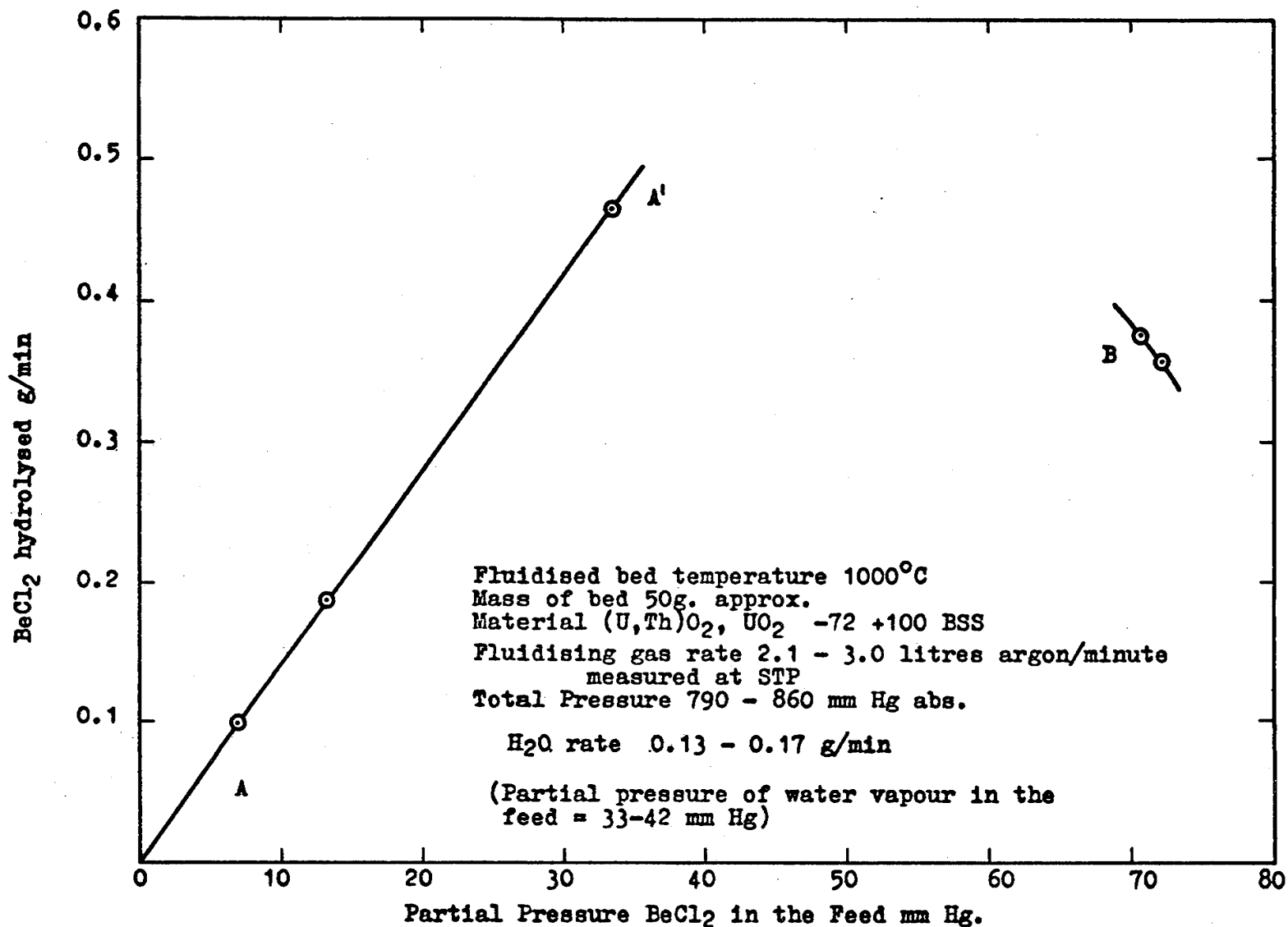


FIGURE 28 RATE OF REACTION OF BERYLLIUM CHLORIDE AT 1000°C

graph of the rate of hydrolysis of beryllium chloride at 1000°C as a function of the partial pressure of beryllium chloride in the feed to the fluidised bed. The reaction rate apparently passes through a maximum value as the partial pressure of beryllium chloride increases beyond the line AA' and subsequently decreases to the points B. A similar curve can be obtained for the hydrolysis of aluminium chloride at 1000°C . These curves are of the same type as those given for initial reaction rate as a function of mole fraction of the reactant by Yang and Hougen (58) for bimolecular gaseous reactions at a surface where either surface reaction or desorption of a reaction product is controlling, and for a non-catalytic homogeneous gas phase reaction.

Operation of the fluidised bed apparatus in runs where the gas inlet tube broke during the run and allowed the water vapour to by-pass the bed (Run A46-II) indicated that hydrolysis of aluminium chloride occurred to essentially the same extent although presumably no oxide was deposited as coating after the break. The presence of the fuel particles is therefore not required for reaction to occur. This suggests that the hydrolysis reaction is not catalysed by the surface of the particles, although a surface reaction could still be responsible for coating buildup. The formation

of dust which is carried from the bed is in accordance with the existence of a homogeneous gas phase reaction.

6.2 Coating Properties

6.2.1 Best Coating Conditions

Coating properties have been shown to be a function of coating temperature, reactant feedrate ratio, and coating rate. For the coating temperatures investigated, the best conditions of coating deposition have been determined. For coating temperatures in the range 500 to 1100°C, best alumina coatings were deposited at 1000°C with an aluminium chloride/water vapour molar feedrate ratio of approximately 0.36 and a maximum coating rate of 2 to 3 microns per hour. At a coating temperature of 1000°C, best beryllia coatings were deposited using a beryllium chloride/water vapour feedrate ratio of approximately 0.5 and a maximum coating rate of about 3 microns per hour. Preliminary beryllia coating runs at 1400°C failed to produce uniform dense coatings, but indicated the possibility of satisfactory coating deposition at this temperature.

These results are in general agreement with information reported by BMI workers and reviewed in Chapter 2. However no data have been published previously indicating an effect of reactant feedrate ratio and coating rate on coating properties. At a coating temperature of 1000°C, Blocher (23) reported no apparent difference in the microstructure

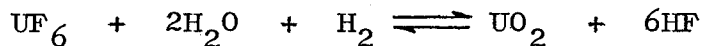
of alumina coatings deposited at 4 microns per hour and at lower rates, but no information was given for higher coating rates. Beryllium chloride/water vapour feedrate ratios in the range 0.67 to 2.0 had no significant effect on the properties of beryllia coatings deposited at 1400°C (30).

The evaluation results obtained for the alumina coated fuel particles are comparable with the published data and confirm the potential of alumina coated fuel particles for use in ceramic nuclear fuels. All beryllia coatings deposited at 1000°C were porous and failed to protect the substrate in evaluation tests. Heat treatment at 1500°C in nitrogen for two hours did not significantly improve their properties. Initial beryllia coating runs at 1400°C failed to produce uniform dense coatings, but the possibility of depositing dense coatings at this temperature was indicated.

6.2.2 Effect of Reactant Feedrate Ratio

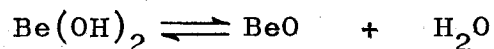
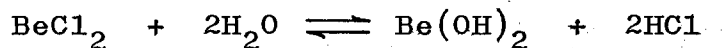
The optimum reactant ratios determined in this investigation correspond to 80 to 100 per cent excess water vapour based on the stoichiometric requirements for the hydrolysis reactions. Similar results have been reported by Knudsen et al (49) for the preparation of uranium dioxide particles by the simultaneous reaction of steam and hydrogen with uranium hexafluoride. They found that, at 700°C in the presence of a large excess of hydrogen, particles with the highest density were obtained in runs where the excess

steam used was in the range 75 to 140 per cent of the stoichiometric requirement based on the reaction

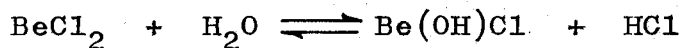


Material of lower density was produced in runs in which a small amount of steam or a large amount of steam was employed. These results agree surprisingly for such different reaction systems and indicate the importance of the ratio of the reactants on the properties of the deposited material.

This effect can possibly be explained in terms of the formation of intermediate products in the hydrolysis reactions which subsequently decompose to give the oxide, with corresponding density changes, after further layers of coating have been deposited. For example, in the presence of a large excess of water vapour the hydrolysis of beryllium chloride could produce beryllium hydroxide which subsequently decomposes to beryllium oxide in the following manner.



Similarly, an excess of beryllium chloride could result in the formation of beryllium oxychloride, which could then decompose to beryllium oxide thus -



Between these two extremes, the optimum conditions exist where the effect of the subsequent decomposition of the intermediate products, if they exist at these conditions, is least pronounced.

6.2.3 Effect of Temperature

The effect of deposition temperature on coating properties can also be explained on a similar basis. Changes in the reaction equilibria with temperature could influence the formation and decomposition of intermediate products. An alternative explanation of Dayton et al (32) suggests that recrystallisation of the coating material in the as-deposited condition to give a dense coating may occur more readily at higher temperatures. With further increases in coating temperature, grain growth effects adversely affect coating integrity.

6.2.4 Effect of Coating Rate

The porosity of coatings produced at higher coating rates may be explained in terms of crystal growth effects. Under conditions of rapid coating deposition, interaction between growing crystallites of the coating material could occur, producing enclosed porosity within the coating. At lower coating rates however, more ordered growth occurs to give a uniformly dense coating.

6.2.5 Effect of Coating Impurities

The presence of uranium contamination in the coatings has been established, and intermediate acid cleanup steps were successful in minimising this problem in alumina coatings built up in a number of runs. The uranium contamination is attributed to the attrition of particles before the commencement of coating deposition and the breakage of occasional particles in the fluidised bed, followed by incorporation of the uranium dioxide dust in the coating as it builds up.

The presence of silicon and residual chloride ion impurities in the coatings could not be correlated with operating variables, or in general with the properties of the deposited coatings. However the 16 per cent silicon contamination in the beryllia coatings produced in Run B5-I was apparently responsible for the improved performance of these coated particles in evaluation tests. More data are needed to elucidate these effects. Silicon contamination is attributed to random impurity contents in the aluminium chloride and beryllium chloride feed materials, with some contribution from corrosion of the vycor apparatus. The presence of residual chloride ions can be accounted for as intermediate reaction products or adsorbed beryllium chloride which was trapped in the coating as further deposition occurred.

The presence of impurity atoms or molecules during coating deposition will produce imperfections in the growing coating which serve as nucleation sites for further crystallites. Thus in the presence of only small amounts of impurities, the growth of a crystallite may proceed uninterrupted by further nucleation to give large columnar grains as reported in Chapter 2. Alternatively if a large number of impurity atoms are present, new crystallites will be nucleated frequently and the average crystallite size for the coating will be much smaller.

6.3 Mechanism of Coating Deposition

The limited data available for the performance of the fluidised bed and the kinetics of the hydrolysis reactions do not permit the determination of the mechanism of coating deposition, although explanations of the type set out in Chapter 2 can be proposed which are in accordance with the experimental data. These proposals have been indicated in the preceding Sections in the discussion of the experimental results and are summarised here.

It can be hypothesised that a homogeneous gas phase reaction producing dust and a heterogeneous non-catalysed surface reaction accounting for coating deposition occur. Alternatively, the hydrolysis reaction may occur solely in the gas phase followed by migration of some of the oxide product, or intermediate reaction products, to the surface of

the particles where nucleation and crystal growth occur to produce the coating. In either case, the proportion of oxide deposited as coating is a function of the quality of fluidisation and the solids-gas contact in the fluidised bed.

Variation in coating properties with the reactant conditions can be attributed to changes in the equilibria of the reactions and the formation of intermediate reaction products. The effects of increased coating rate on coating porosity and the presence of impurities on crystallite size can be accounted for by classical nucleation and crystal growth theory in terms of interactions between growing crystallites at high coating rates and the nucleation of new crystallites by impurity atoms during coating deposition.

CHAPTER 7SUMMARY AND CONCLUSIONS

Alumina and beryllia coatings have been deposited on UO_2 and $(\text{U,Th})\text{O}_2$ particles by the technique of chemical vapour deposition in a fluidised bed. Hydrolysis of aluminium chloride and beryllium chloride with water vapour were selected as the reaction systems. Coating properties were evaluated by metallographic examination, Knoop hardness measurements, acid-leach and air-oxidation testing, measurement of alpha-particle emission, chemical analysis, heat treatment, and fission gas release measurements on post-irradiation annealing. Coating integrity was shown to be a function of coating temperature, reactant feedrate ratio, and coating rate.

For coating temperatures in the range 500 to 1100°C, best alumina coatings were deposited at 1000°C with an $\text{AlCl}_3/\text{H}_2\text{O}$ molar feedrate ratio of approximately 0.36 and a maximum coating rate of 2 to 3 microns per hour. The alumina coatings deposited under these conditions were dense and translucent with Knoop hardnesses of up to 3200 kg/mm². The evaluation results obtained were consistent with published data and confirmed the promise of alumina coated fuel particles for use in ceramic nuclear fuels.

At a coating temperature of 1000°C , best beryllia coatings were deposited using a $\text{BeCl}_2/\text{H}_2\text{O}$ molar feedrate ratio of about 0.5 and a maximum coating rate of about 3 microns per hour. All beryllia coatings produced at 1000°C were porous, and heat treatment at 1500°C in nitrogen for two hours did not significantly improve their properties. Initial beryllia coating runs at a fluidised bed temperature of 1400°C failed to produce uniform dense coatings, but indicated the possibility of satisfactory coating deposition at this temperature.

Explanations for possible mechanisms of coating deposition have been proposed. Coating deposition may occur as a result of a heterogeneous non-catalytic surface reaction or a homogeneous gas-phase reaction followed by transport of the oxide product, or intermediate reaction products, to the surface of the particles where nucleation and crystal growth occurs. The proportion of oxide deposited as coating is a function of the solids-gas contact in the fluidised bed. Variations in coating properties with the conditions of deposition may be explained by changes in the equilibria of the reactions, the formation of intermediate reaction products, and by crystal growth theory. Determination of the mechanism of coating deposition is a subject for much further investigation which will need to take

into consideration the mechanism and kinetics of the hydrolysis reactions and the complex heterogeneity of a gas-solids fluidised bed.

Further work is required to determine optimum conditions of deposition for beryllia coatings. Long term irradiation testing of both alumina and beryllia coated particles, in the as-produced condition and as fabricated fuel specimens, is necessary to evaluate their fission-product retention characteristics under reactor operating conditions. An analysis of the cost of coated particle preparation will also be required in the final assessment of the coated particle concept.

APPENDIX IFABRICATION OF FUEL PARTICLESI.1 Basic Process

Kilogram quantities of dense, near-spherical particles of UO_2 and $(\text{U,Th})\text{O}_2$ were produced using conventional ceramic processes to provide substrate material for the coated particle work. The processes were essentially similar to that developed by Jones and Reeve (59), and the basic steps are shown in Figure 29. Since uranium and thorium oxides are radioactive and toxic materials, they were contained in powder handling glove boxes maintained at one inch of water pressure below atmospheric conditions during fabrication (Figure 30).

I.2 UO_2 Particles

Natural uranium dioxide powder, nominally -300 BSS Mallinckrodt Ceramic Grade, was compacted at 8 tsi into pellets $3/4$ inch diameter and $3/8$ inch high in a steel die using a small hand press, or, in later stages of the experimental work, into pellets 4 inch diameter and 1 inch high in steel dies using a 1000 ton press. The pellets were reduced to $-1/4$ inch in a mortar and pestle, crushed in a Glen Creston micro-hammer mill and sieved to a size about 20 per cent greater than finally required. Rounding by vibratory shaking gave yields of approximately 70 per cent

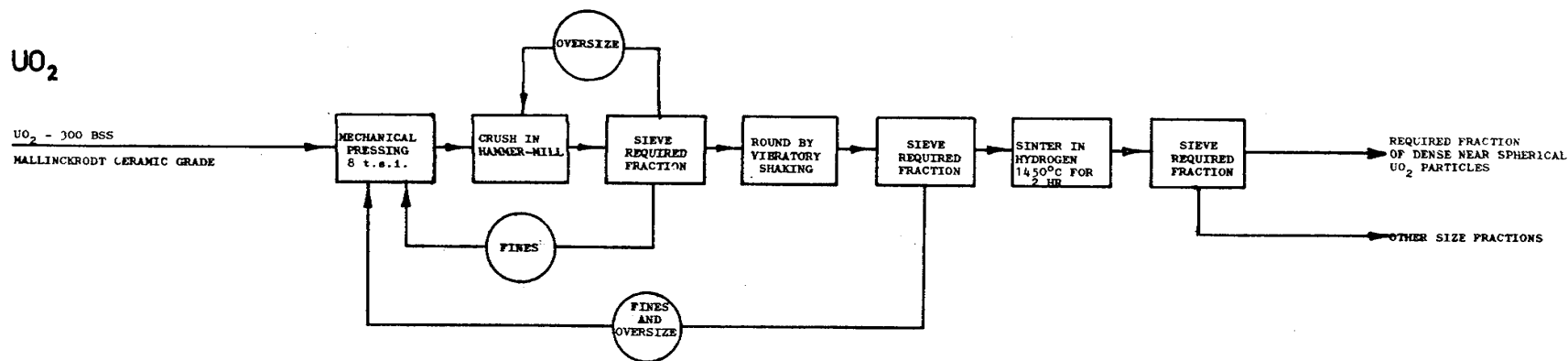
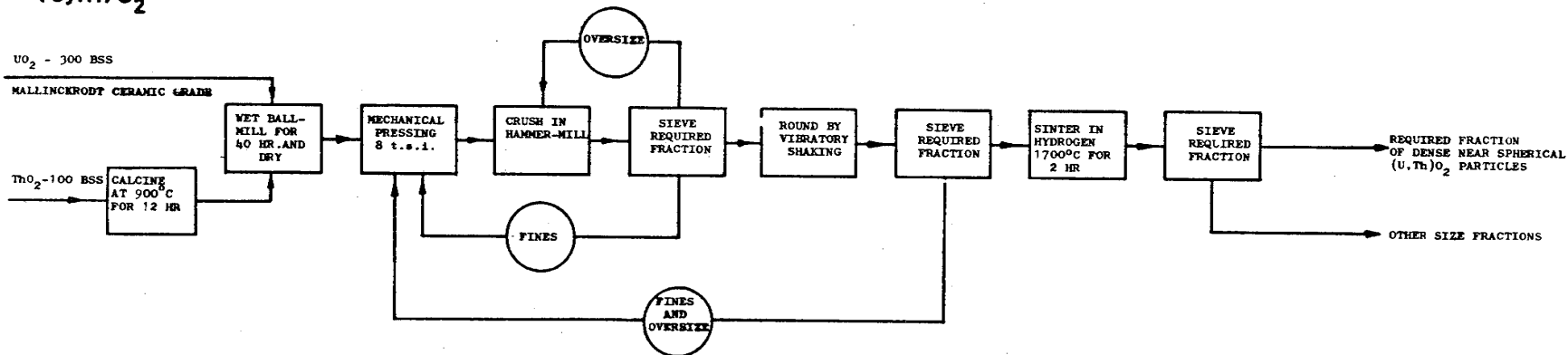
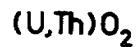


FIGURE 29. PRODUCTION OF DENSE NEAR SPHERICAL FUEL PARTICLES.



Figure 30 - Powder Handling Glove Boxes

of near-spherical particles. The rounded UO_2 particles were sintered, in alumina trays filled to a depth of 1/2 inch, for 2 hours in a hydrogen atmosphere at 1450°C , using a molybdenum-wound resistance furnace. Hydrogen was used as the blanket gas over the molybdenum winding. The sintered particles were sieved giving yields of particles in the required size range of approximately 70 to 80 per cent with densities of 95 to 97 per cent of the theoretical 10.95 g/cm^3 , measured with an S.G. bottle using xylene as the immersion liquid. Figure 31 shows the particles produced.

I.3 (U,Th) O_2 Particles

Fuel particles of $(\text{U,Th})\text{O}_2$ with an atomic ratio of U:Th of 1:50 and 1:20 were fabricated by a similar route. Thoria powder calcined at 900°C for 12 hours was wet ball-milled with uranium for up to 40 hours in a polythene jar using alumina grinding balls. This milling operation broke up aggregates of UO_2 and ThO_2 and dispersed individual UO_2 and ThO_2 particles to give a fine and uniform mixture. The degree of mixing was considered satisfactory if no particles of UO_2 and ThO_2 of more than 10 microns in diameter could be distinguished at a magnification of 100, and if the majority of particles were less than 5 microns in diameter. Following pressing, crushing, rounding, and sieving, particles in the required size range were sintered in hydrogen for 2 hours at

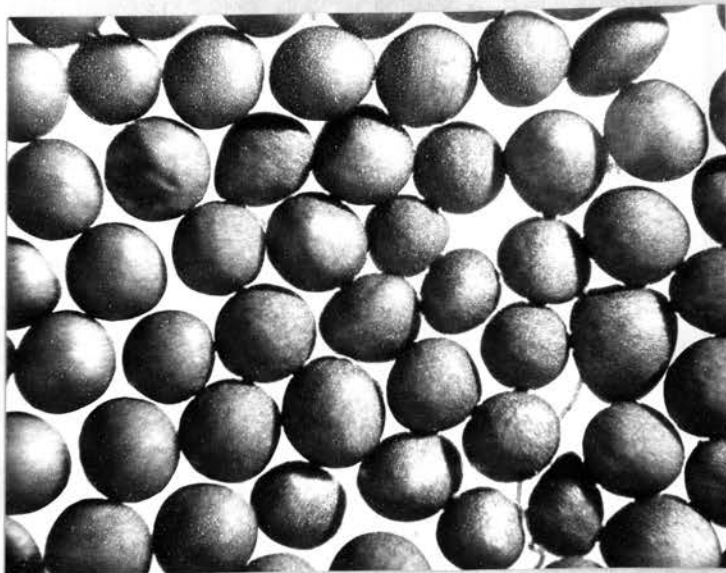


Figure 31 - UO_2 Particles -72+100 BSS

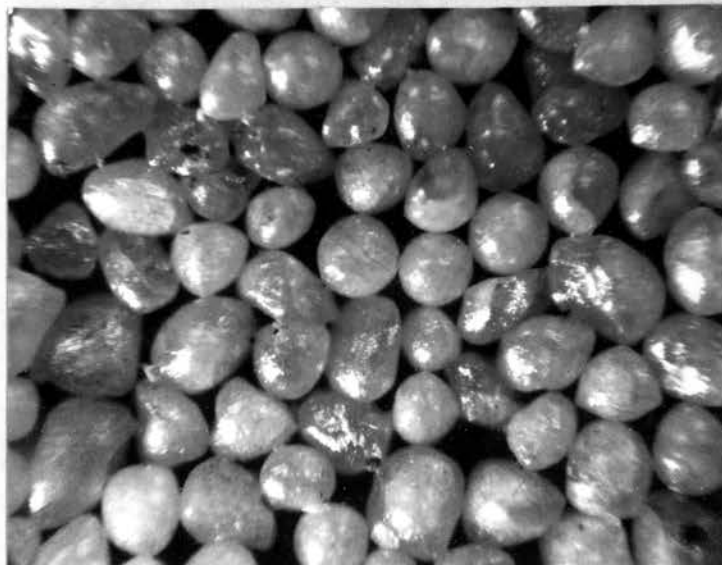


Figure 32 - $(\text{U,Th})\text{O}_2$ Particles -72+100 BSS

1700°C to give densities of 95-98 per cent theoretical.

Figure 32 shows the particles produced.

Examination of metallographically polished, sintered (U,Th)O₂ particles (U:Th::1:20) by an electron probe micro-analyser showed that the U:Th ratio was uniform from particle to particle, and on the 5 micron scale in any one particle, the variation in the nominal composition was $\pm 5\%$. Since the grain size of the particles was about 25 microns, this means the uranium dioxide and thorium dioxide were present as a near homogeneous solid solution.

APPENDIX IIPREPARATION OF BERYLLIUM CHLORIDE

Some of the beryllium chloride required for beryllium oxide coating studies was produced by the method of direct chlorination of beryllium turnings in a static bed, developed by Carter (60).

II.1 Apparatus

Figure 33 is a diagram of the apparatus. The equipment was located in a glove box because of the toxicity hazards of beryllium and its compounds. Argon and chlorine were fed through metering equipment and a non-return valve to the silica reactor. A mercury manometer pressure relief device was provided. The reactor was heated by a nichrome wound resistance furnace. The beryllium chloride was condensed into the vapouriser used in the coating experiments, to avoid moisture pickup during transfer of the hygroscopic material. The condenser was maintained at 250 to 280°C by means of a second nichrome wound resistance furnace. A "hot finger", consisting of a nichrome resistance heater, prevented condensation of the beryllium chloride in the connexion between the reactor and the condenser. The excess chlorine was scrubbed from the inert gas with 25 wt per cent caustic soda solution, and the inert gas discharged to the exhaust

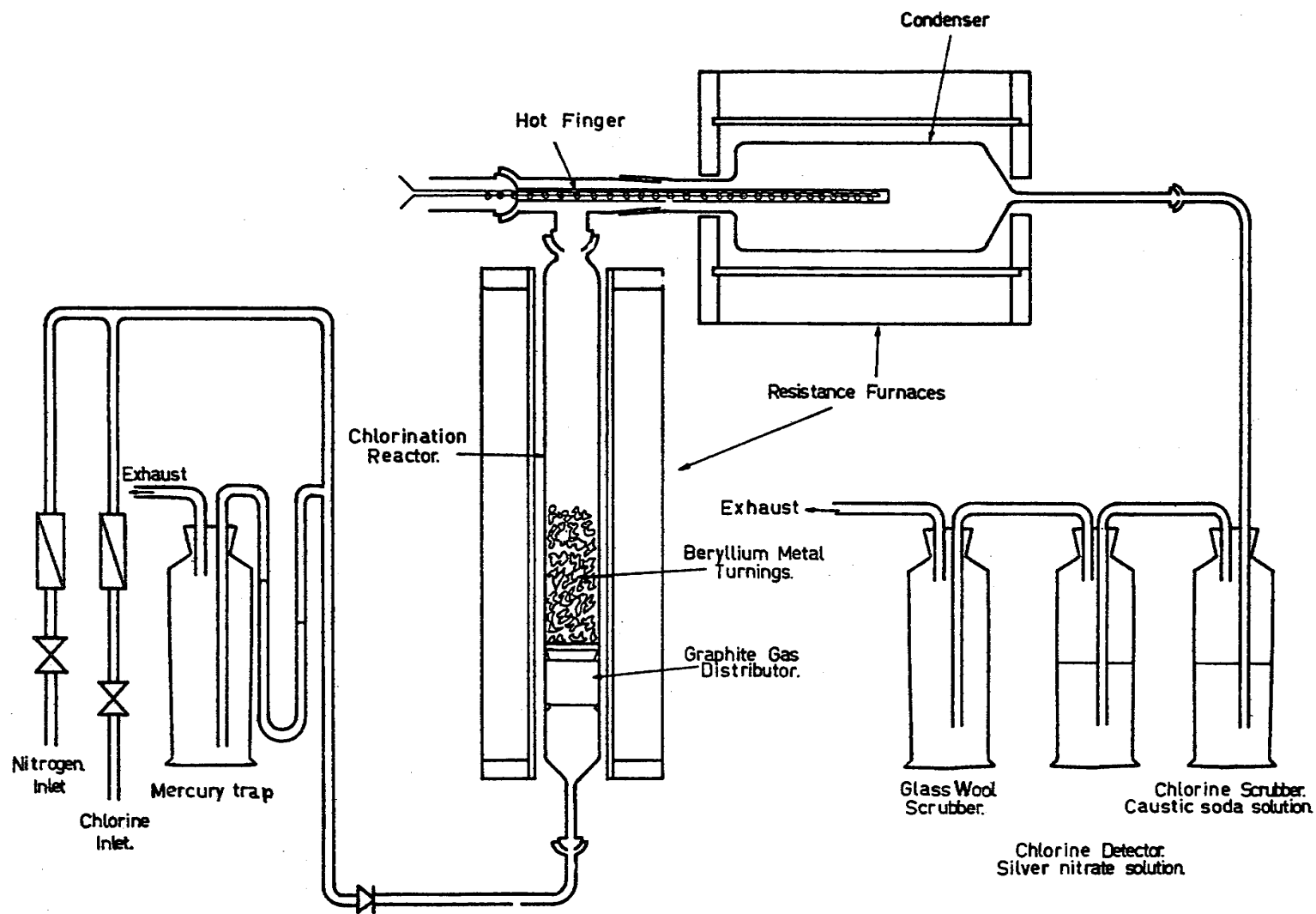


FIGURE 33. APPARATUS FOR THE PREPARATION OF BERYLLIUM CHLORIDE.

system. This scrubber also indicated the completion of reaction. When the reaction ceased, an increase in bubbling rate due to the presence of unreacted chlorine was observed in this scrubber.

II.2 Procedure

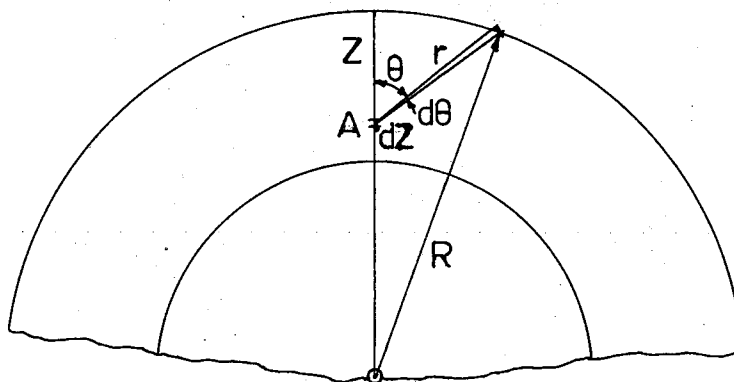
Approximately 10 grams of beryllium metal turnings were loaded into the reactor, and the equipment assembled. The apparatus was flushed with nitrogen at 0.5 l/min and the reactor heated to 600°C. The chlorine was then fed to the reactor at 0.3 l/min and the nitrogen rate reduced to 0.3 l/min. When the chlorination commenced, the heat of reaction was sufficient to maintain further reaction. The reaction temperature was controlled below 900°C by reducing the chlorine flowrate as required. When the reaction was complete, the chlorine was shut off and the nitrogen continued to pass through the apparatus to carry over any low boiling point chloride impurities from the condenser.

The beryllium chloride condensed as a dense needle-like crystalline mass. The yields of beryllium chloride obtained corresponded to approximately 90 per cent chlorination of the beryllium turnings.

APPENDIX IIIALPHA PARTICLE EMISSION FROM COATED
FUEL PARTICLES

This derivation gives a method of calculating the proportion of the total alpha particles emitted by uranium atoms in the outer thickness of the coating, equivalent to the alpha range in the coating material, which will escape from the coating. The alpha emission rate determined with the scintillation counter can then be corrected to give the total alpha particle emission rate.

Consider a coated fuel particle with a coating thickness greater than the range ρ of an alpha particle in the coating material, and an outer radius R .



Consider alpha emission of an element dz at a point A in the coating which is distance Z from the surface, where $Z < \rho$.

- Assume (1) Alpha emission at any point in the coating is isotropic.
- (2) The range of all alpha particles is equal.
- (3) Alpha emission occurs throughout the coating due to uniform contamination of the coating.
- (4) No absorption of alpha-particles occurs in contaminant particles.

For an element of surface subtending $d\theta$ at point A and distance r from A,

fractional solid angle subtended at A by a circular element of width $r d\theta$ and radius $r \sin\theta$

$$= \frac{2\pi r \sin \theta \, r d\theta}{4\pi r^2}$$

$$= \frac{\sin \theta \, d\theta}{2}$$

To determine the fraction of alpha-particles emitted in the coating which actually escape from the surface of the coating, this expression needs to be integrated for the range of -

$$\theta = 0 \text{ to } \theta = \theta_L \quad \text{where } r = \rho$$

and for

$$Z = 0 \text{ to } Z = \rho$$

For point A, the fraction of all alpha-particles emitted which actually escape from the surface of the coating is

$$\int_0^{\theta_L} \frac{\sin \theta}{2} d\theta \quad \text{where } \theta_L = \text{the value of } \theta \text{ when } r = \rho$$

Integrating this expression for all values of Z to account for all alpha-particles emitted within a shell at the surface which is ρ in thickness,

$$\text{total fraction of alpha particles escaping} = \frac{\int_0^{\rho} \int_0^{\theta_L} \frac{\sin \theta}{2} d\theta dz}{\int_0^{\rho} dz}$$

Expressing θ_L in terms of ρ, R, Z

$$R^2 = \rho^2 + (R-Z)^2 + 2(R-Z)\rho \cos \theta_L$$

$$\therefore \theta_L = \cos^{-1} \frac{2ZR - \rho^2 - Z^2}{2(R-Z)\rho}$$

Hence, total fraction of alpha particles released

$$\begin{aligned} &= \frac{1}{2\rho} \int_0^{\rho} \left[-\cos \theta \right]_0^{\theta_L} dz \\ &= \frac{1}{2\rho} \int_0^{\rho} \left[1 - \frac{2ZR - \rho^2 - Z^2}{2(R-Z)\rho} \right] dz \\ &= \frac{1}{2\rho} \left[\frac{3\rho}{4} + \frac{R}{2} + \left\{ \frac{R^2}{2\rho} - \frac{\rho}{2} \right\} \log_e \frac{R-\rho}{R} \right] \end{aligned}$$

Sample Calculation:

For Run A43-VI, the size range of the UO_2 particles is -72+100 BSS, that is 152-211 microns.

- $\therefore$ Mean UO_2 particle diameter = 182 microns
 Coating thickness = 40 microns $\therefore$ Table 2
 $\therefore$ Mean outer radius of the coated particle = R = 131 microns
 Range of an alpha particle in alumina = ρ = 10 microns

Hence, substituting in the above equation,

$$\begin{array}{l} \text{fraction of alpha particles} \\ \text{released from the outer 10} \\ \text{microns of alumina coating} \end{array} = 0.26$$

Therefore the total number of alpha particles emitted by uranium atoms in the outer 10 microns of coating = $\frac{1}{0.26} = 3.85$ times the alpha emission rate measured with the scintillation counter.

APPENDIX IVEXPERIMENTAL DATA

Tables 2, 3, 4, 5 and 6 give a summary of the experimental data concerning the preparation and evaluation of the alumina and beryllia coated fuel particles.

Table 2 Primary Experimental Data for the Alumina
 Coated Fuel Particles

Table 3 Evaluation Data for the Alumina Coated
 Fuel Particles

Table 4 Acid leach Data for Alumina Coated (U,Th)O₂
 Particles

Table 5 Primary Experimental Data for the Beryllia
 Coated Fuel Particles

Table 6 Evaluation Data for the Beryllia Coated
 Fuel Particles

TABLE 2 - PRIMARY EXPERIMENTAL DATA FOR THE ALUMINA COATED FUEL PARTICLES

Run	Fuel Particles				Mass of Bed g	Temperature of Bed °C	Reactant Conditions					Time of Run hours	Analysis of coated Particles % by wt Al ₂ O ₃	Partic-les coated and re-covered %	Material balance on fuel %	Conversion Efficiency %	Bed Efficiency %	Coating Thick-ness microns	Coating Rate		Comments
	Material	Lot No.	Density g/cc	Particle size B.S.S.			Argon Rate l/min. S.T.P.	AlCl ₃ rate g/min.	H ₂ O rate g/min.	AlCl ₃ /H ₂ O mole ratio	Average Total Pressure mm Hg abs.								microns per hour	g/(hr of bed)	
A1-I	UO ₂	14	9.87	-100+150	45	950	2.55	0.58	0.12	0.65	790	0.75	-	-	-	66	-	5	6.7	-	No sample retained
A1-II	-	-	-	-	47	950	2.35	0.26	0.13	0.27	810	5.0	36.4	75	-	88	-	20	3.0	-	
A2-I	(U,Th)O ₂	42,47	9.73	-44+72	59.8	750	4.6	0.31	0.13	0.32	860	4.5	21.9	84.5	-	73	43	32	7.1	0.062	
A3-I	(U,Th)O ₂	40,43 48	9.72	-72+100	48.2	1000	3.15	0.72	0.22	0.44	830	2.25	17.9	91.5	-	74	26	20	8.9	0.10	
A4-I	(U,Th)O ₂	63	9.63	-72+100	46.5	1000	2.35	0.48	0.11	0.59	880	3.5	28.7	89.2	-	85	43	17	4.9	0.11	
A5-I	(U,Th)O ₂	72	9.84	-72+100	50.0	900	3.2	0.35	0.10	0.47	810	4.5	18.5	84.0	-	55	26	9	2.0	0.050	
A6-I	(U,Th)O ₂	66	9.68	-72+100	45.8	1050	2.8	0.80	0.12	0.90	820	2.0	12.5	88.5	-	21	16	3	1.5	0.07	
A7-I	(U,Th)O ₂	56,74	9.86	-72+100	48.2	1050	2.85	1.16	0.13	1.2	820	1.25	14.0	77.7	-	23	18	3	2.0	0.13	
A8-I	(U,Th)O ₂	74,77	9.83	-72+100	49.0	1000	3.0	0.31	0.12	0.35	810	3.25	44.2	-	-	82	-	65	20	0.24	
A9-I	(U,Th)O ₂	77,79	9.83	-72+100	50.5	900	2.85	0.66	0.23	0.39	810	3.0	16.8	86.5	-	34	20	31	10.3	0.067	
A10-I	(U,Th)O ₂	70,81	9.79	-72+100	50.3	700	3.0	0.50	0.12	0.56	810	4.0	21.9	67	-	33	20	32	8.0	0.070	No sample retained
A11-I	(U,Th)O ₂	86	9.80	-72+100	50.1	1000	3.1	0.17	0.13	0.18	800	4.25	14.3	94.1	94.1	85	48	10	2.4	0.040	
A12-I	(U,Th)O ₂	86,89 91	9.88	-72+100	51.6	1000	2.85	0.20	0.12	0.22	840	5.0	20.4	88.0	88.0	65	51	6	1.2	0.051	
A12-II	-	-	-	-	50.1	1000	3.0	0.25	0.12	0.28	830	5.0	35.0	89.5	-	74	35	13	1.4	0.044	
A13-I	(U,Th)O ₂	94,97	9.95	-72+100	50.1	1000	1.6	0.13	0.05	0.35	810	1.0	2.30	99.0	99.0	99	39	1	1	0.027	
A13-II	-	-	-	-	49.2	1000	2.65	0.29	0.033	1.18	840	4.0	10.0	90	-	43	20	8	2.0	0.028	
A14-I	(U,Th)O ₂	102,105 107	9.83	-72+100	97.3	1000	2.30	0.3	0.042	0.96	820	2.0	-	-	-	38	-	2	1	-	
A14-II	-	-	-	-	98.2	1000	2.45	0.63	0.06	1.42	840	1.75	4.4	-	-	21	(17)	4	1.1	-	
A15-I	UO ₂	163	10.74	-72+100	50.3	1000	2.50	0.29	0.064	0.61	810	3.5	10.0	96.0	97.0	62	23	7	2.0	0.032	
A16-I	UO ₂	168	10.74	-72+100	50.7	1000	2.55	0.17	0.046	0.50	830	4.0	10.9	95.2	97.8	90	39	8	2.0	0.031	
A17-I	UO ₂	163,168 171	10.71	-72+100	50.1	1000	2.70	0.36	0.050	0.97	810	3.0	9.6	81.2	95.8	41	18	3	1.0	0.035	No sample retained
A18-I	UO ₂	171	10.60	-72+100	50.3	1000	2.55	0.11	0.048	0.31	830	3.5	5.9	99.2	100.0	100	36	6	1.7	0.018	
A19-I	UO ₂	174	10.68	-72+100	50.4	1000	2.50	0.21	0.078	0.36	880	6.0	17.1	98.8	99.8	89	36	12	2.0	0.034	
A20-I	UO ₂	174,180	10.71	-72+100	50.7	1000	2.60	0.18	0.067	0.36	870	5.0	12.0	99.2	100.6	94	33	10	2.0	0.030	
A21-I	UO ₂	180,183	10.73	-72+100	50.2	1000	2.75	0.18	0.070	0.35	820	5.33	12.4	95.0	100.0	95	31	14	2.6	0.027	
A22-I	UO ₂	183,189	10.78	-72+100	51.0	1000	2.90	0.14	0.79	0.24	810	4.0	7.7	98.8	99.4	93	33	6	1.5	0.021	
A23-I	UO ₂	192	10.74	-72+100	50.8	1000	2.70	0.20	0.081	0.33	820	2.66	8.0	96.0	98.1	96	34	10	3.8	0.033	
A 3-II	-	-	-	-	52.8	1000	2.60	0.24	0.077	0.42	800	3.25	22.7	97.8	97.8	85	53	17	2.2	0.059	
A23-III	-	-	-	-	50.0	1000	2.90	0.22	0.083	0.36	810	5.0	33.8	99.5	99.8	88	34	34	3.4	0.034	
A23-IV	-	-	-	-	49.8	1000	2.80	0.20	0.078	0.35	810	5.25	44.5	99.4	99.7	92	37	43	1.7	0.036	
A24-I	UO ₂	192	10.74	-72+100	50.5	1000	2.65	0.22	0.16	0.18	810	3.0	7.1	100.0	100.0	86	25	5	1.7	0.025	No sample retained
A25-I	UO ₂	192	10.74	-72+100	50.0	1000	2.65	0.29	0.14	0.28	840	2.75	11.1	97.8	97.8	89	34	17	6.2	0.045	
A26-I	UO ₂	192	10.74	-72+100	50.2	1000	2.85	0.34	0.44	0.104	800	3.75	19.1	101.5	101.5	62	42	35	9.3	0.063	

TABLE 2 (Continued)
PRIMARY EXPERIMENTAL DATA FOR THE ALUMINA COATED FUEL PARTICLES

Run	Fuel Particles				Mass of Bed g	Temperature of Bed °C	Reactant Conditions					Time of Run hours	Analysis of coated particles % by wt Al ₂ O ₃	Particles coated and recovered %	Material balance on fuel %	Conversion Efficiency %	Bed Efficiency %	Coating Thickness microns	Coating Rate		Comments
	Material	Lot No.	Density	Particle Size B.S.S.			Argon rate l/min. S.T.P.	AlCl ₃ rate g/min.	H ₂ O rate C/min.	AlCl ₃ /H ₂ O mole ratio	Average Total Pressure mm Hg abs.								microns per hour	g/(hr of bed)	
A27-I	UO ₂	194	10.74	-72+100	49.7	1000	2.75	0.46	0.19	0.33	810	2.75	21.7	88.2	88.2	87	42	16	5.8	0.10	
A28-I	UO ₂	205	10.76	-72+100	50.1	900	2.90	0.22	0.076	0.39	800	4.17	14.5	95.8	96.7	94	40	17	4.1	0.040	
A29-I	UO ₂	205	10.76	-72+100	50.5	700	2.55	0.21	0.085	0.33	800	2.83	13.1	97.6	97.8	84	56	15	5.3	0.053	
A30-I	UO ₂	205	10.76	-72+100	50.3	500	2.75	0.23	0.081	0.38	810	2.67	11.3	98.2	98.2	78	44	13	4.9	0.048	
A31-I	UO ₂	205	10.76	-72+100	50.2	500	2.80	0.19	0.073	0.35	830	4.0	18.3	85.4	85.8	89	56	18	4.5	0.056	
A32-I	UO ₂	207	10.45	-72+100	51.0	900	2.75	0.21	0.065	0.43	830	5.0	17.3	97.4	97.9	81	43	17	3.4	0.042	
A33-I	UO ₂	207	10.45	-72+100	100.1	1000	2.80	0.23	0.081	0.38	820	3.92	7.8	99.3	99.5	90	41	6	1.5	0.022	
A34-I	UO ₂	207	10.45	-72+100	149.3	1000	2.75	0.22	0.081	0.37	840	4.0	5.5	98.8	99.3	89	42	4	1.0	0.0146	
A35-I	UO ₂	209	10.59	-72+100	49.8	900	2.85	0.23	0.080	0.39	810	5.0	23.0	92.4	95.6	85	51	25	5.0	0.060	
A36-I	UO ₂	209	10.59	-72+100	50.4	1000	1.88	0.21	0.080	0.35	880	1.33	5.1	99.2	99.4	93	41	4	3.0	0.040	
A37-I	UO ₂	209	10.59	-72+100	50.0	1000	3.65	0.24	0.076	0.43	810	2.42	9.7	76.8	97.0	90	31	14	5.8	0.044	
A38-I	UO ₂	209	10.59	-72+100	50.4	1000	2.40	0.20	0.080	0.34	790	3.17	9.9	98.8	99.4	91	37	8	2.5	0.035	
A39-I	UO ₂	209	10.59	-72+100	49.8	700	2.85	0.19	0.10	0.26	810	4.0	14.7	99.6	100.8	90	50	21	5.2	0.043	
A40-I	UO ₂	211	10.39	-72+100	50.2	700	2.80	0.19	0.087	0.29	800	2.5	4.0	96.6	98.0	91	20	10	4.0	0.017	
A41-I	UO ₂	211	10.39	-72+100	50.0	1100	2.58	0.30	0.115	0.35	830	1.67	7.0	98.6	98.6	89	33	5	3.0	0.045	
A42-I	UO ₂	273	10.34	-72+100	50.6	1100	2.54	0.22	0.096	0.31	840	4.17	14.4	100.8	101.2	96	41	11	3.8	0.040	
A43-I	UO ₂	273	10.34	-72+100	51.0	1000	2.73	0.21	0.080	0.35	800	3.5	10.6	95.2	95.8	90	35	-	-	0.034	
A43-II	-	-	-	-	49.0	1000	2.74	0.23	0.080	0.39	800	1.5	15.8	100.0	99.8	69	37	-	-	0.042	
A43-III	-	-	-	-	50.2	1000	2.73	0.31	0.095	0.44	820	1.83	21.0	99.8	98.6	79	24	15	-	0.035	
A43-IV	-	-	-	-	49.6	1000	2.62	0.25	0.086	0.39	810	3.67	29.1	98.8	99.8	64	26	-	-	0.031	
A43-V	-	-	-	-	50.3	1000	2.78	0.23	0.081	0.38	810	3.0	40.2	94.0	94.4	87	55	-	-	0.044	
A43-VI	-	-	-	-	49.4	1000	2.61	0.27	0.078	0.28	830	3.83	46.2	101.3	101.7	71	24	40	-	0.029	
A44-I	UO ₂	270	10.38	-72+100	50.0	1000	2.75	0.22	0.081	0.37	820	5.17	17.1	96.0	96.2	92	38	12	2.4	0.040	
A45-I	(U,Th) ₂ O ₇	259	9.56	-72+100	50.5	1000	2.66	0.22	0.084	0.35	800	4.17	15.4	96.7	97.3	93	42	13	3.1	0.044	
A46-I	-	259	9.56	-72+100	50.0	1000	2.54	0.21	0.078	0.36	830	3.0	9.8	90.2	90.4	95	37	-	-	0.036	
A46-II	-	-	-	-	49.3	1000	2.64	0.21	0.073	0.39	820	4.33	12.0	98.5	98.5	90	9	-	-	0.006	H ₂ O inlet tube broke during run
A47-I	UO ₂	-	-	-72+100	50.0	1000	1.74	0.22	0.085	0.35	860	4.0	12.8	98.4	98.6	95	36	-	-	0.037	
A48-I	UO ₂	312	-	-72+100	50.5	1000	3.10	0.21	0.081	0.35	830	4.0	10.6	103.4	103.6	92	32	-	-	0.030	
A49-I	(U,Th) ₂ O ₇	219,310	9.50	-72+100	200.0	1000	2.47	0.23	0.089	0.35	890	3.0	2.93	98.9	99.5	78	46	-	-	-	

TABLE 3

EVALUATION DATA FOR THE ALUMINA COATED FUEL PARTICLES

Run	Knoop Hardness kg/mm ²	Acid Leach 7.5M HNO ₃ 1st 6 hours		Acid Leach 7.5M HNO ₃ 2nd 6 hours		U as surface contamination		Chemical Analysis of Coatings			
		U diss. %	Al diss. %	U diss. %	Al diss. %	As pro- duced %	After 12 hours leaching %	Si ppm	Cl ⁻ ppm		
A1-I	-	-	-	-	-	-	-	-	-		
A1-II	-	}	}	}	}	0.05	≤0.005	-	-		
A2-I	310± 40					-	-	-	-		
A3-I	-					-	-	-	-		
A4-I	1420±540					-	-	-	-		
A5-I	-					-	-	-	-		
A6-I	-					-	-	-	-		
A7-I	-					See Table 4		-	-	-	-
A8-I	960±270					-	-	-	-		
A9-I	130± 20					-	-	-	-		
A10-I	90± 20					-	-	-	-		
A11-I	1300±170					-	-	-	-		
A12-I	-					-	-	-	-		
A12-II	2580±710	-	-	-	-						
A13-I	-	-	-	-	-	-	-				
A13-II	-	-	-	-	-	-	-				
A14-I	-	-	-	-	-	-	-				
A14-II	-	-	-	-	-	-	-				
A15-I	1970±730	2.5	0.05	1.9	0.13	-	-	670	1700		
A16-I	2630±540	0.6	0.08	2.7	0.09	-	-	-	-		
A17-I	1290± 90	-	-	-	-	-	-	-	-		
A18-I	2400±680	8.0	0.8	0.8	0.18	-	-	-	-		
A19-I	3100±800	0.40*	0.4	0.1	0.08	-	-	-	-		
A20-I	-	1.0	0.03	0.2	0.1	-	-	-	-		
A21-I	2310±330	4.3	0.13*	0.15	0.015	-	-	300	3200		
A22-I	2070±130	2.4	0.04	0.20	0.009	-	-	920	5600		
A23-I	-	-	-	-	-	-	-	-	-		
A23-II	2600±510	0.25	-	0.049	-	0.4	-	-	-		
A23-III	-	0.047	-	0.003	-	0.02	0.03	-	-		
A23-IV	-	0.023*	-	0.0029*	-	0.008	-	650	500		
A24-I	1400±170	19	-	-	-	-	-	-	-		
A25-I	1620±160	3.2	-	1.5	-	0.6	-	-	-		
A26-I	60± 5	70	-	-	-	-	-	-	-		
A27-I	1380±230	0.63	-	0.16	-	-	-	-	-		

* The asterisks indicate acid-leach tests made under agitated conditions. Results of acid-leach tests without agitation have no asterisk.

TABLE 3 (Continued)

EVALUATION DATA FOR THE ALUMINA COATED FUEL PARTICLES

Run	Knoop Hardness kg/mm ²	Acid Leach 7.5M HNO ₃ 1st 6 hours		Acid Leach 7.5M HNO ₃ 2nd 6 hours		U as surface contamination		Chemical Analysis of Coatings	
		U diss. %	Al diss. %	U diss. %	Al diss. %	As pro- duced %	After 12 hours leaching %		
								Si ppm	Cl ⁻ ppm
A28-I	-	-	0.21 *	-	-	-	-	660	980
A29-I	350± 210	-	1.1 *	-	-	-	-	1400	3200
A30-I	640± 170	-	-	-	-	-	-	-	-
A31-I	700± 210	-	54 *	-	-	-	-	1100	12400
A32-I	-	-	-	-	-	-	-	-	-
A33-I	2590± 920	-	-	-	-	-	-	-	-
A34-I	3200± 900	-	-	-	-	-	-	-	-
A35-I	200± 60	-	-	-	-	-	-	-	-
A36-I	1440± 590	-	-	-	-	-	-	-	-
A37-I	780± 170	-	-	-	-	-	-	-	-
A38-I	1990± 330	-	-	-	-	-	-	-	-
A39-I	360± 140	-	-	-	-	-	-	-	-
A40-I	-	-	-	-	-	-	-	-	-
A41-I	-	20.5 *	-	4.5 *	-	-	-	-	-
A42-I	1830± 180	3.5 *	0.20 *	0.64 *	-	-	-	980	-
A43-I	-	-	-	-	-	-	-	-	-
A43-II	-	-	-	-	-	-	-	-	-
A43-III	-	0.38 *	-	0.11 *	-	-	-	-	-
A43-IV	-	0.021 *	-	0.0049 *	-	-	-	-	-
A43-V	-	0.0042 *	-	0.0003 *	-	-	-	-	-
A43-VI	2620± 610	0.016 *	-	0.0014 *	-	<0.003	<0.002	470	240
A44-I	2950± 710	1.4 *	-	0.08 *	-	-	-	800	820
A45-I	2810± 710	-	-	-	-	-	-	-	-
A46-I	-	-	-	-	-	-	-	-	-
A46-II	-	-	-	-	-	-	-	-	-
A47-I	-	-	-	-	-	-	-	-	-
A48-I	-	-	-	-	-	-	-	-	-
A49-I	-	-	-	-	-	-	-	-	-

* The asterisks indicate acid-leach tests made under agitated conditions. Results of acid-leach tests without agitation have no asterisk.

TABLE 4 - ACID-LEACH DATA FOR THE ALUMINA COATED FUEL PARTICLES

Run	Fuel Particle U:Th ratio	Acid leach 0-6 hours 7.5M HNO ₃				Acid leach 6-12 hours 7.5M HNO ₃				Acid leach 0-6 hours 7.5M HNO ₃ + 0.005M F ⁻				Acid leach 6-12 hours 7.5M HNO ₃ + 0.005M F ⁻			
		U diss.	Th diss.	Th/U diss.	Al diss.	U diss.	Th diss.	Th/U diss.	Al diss.	U diss.	Th diss.	Th/U diss.	Al diss.	U diss.	Th diss.	Th/U diss.	Al diss.
		%	%		%	%	%		%	%	%		%	%	%		%
A1-II	-	0.3	-	-	-	0.007	-	-	0.2	0.8	-	-	2.2	1.0	-	-	0.1
A2-I	58	0.3	0.01	2	0.8	0.1	0.001	<1	0.2	6.3	2.3	20	4.3	10	7.2	48	0.2
A3-I	54	0.3	0.08	14	-	0.03	0.001	23	0.08	6.2	4.8	37	1.9	6.4	6.0	45	0.2
A4-I	63	0.2	0.003	1	1.4	0.05	0.002	<2	0.02	2.4	1.0	27	0.34	0.9	0.7	47	0.1
A5-I	60	0.06	0.002	2	0.1	0.02	0.02	86	0.06	7.6	5.2	41	0.15	8.6	5.4	37	0.09
A6-I	56	-	-	-	-	-	-	-	-	13	10	42	0.25	5.2	3.9	43	0.2
A7-I	64	-	-	-	-	-	-	-	-	22	13	37	0.33	16	10	40	1.3
A8-I	58	0.3	0.03	6	0.5	0.08	0.15	111	0.03	20	14	42	0.14	31	24	44	0.9
A9-I	63	0.6	0.02	2	1.5	0.3	0.01	2.2	0.5	13	6.8	33	7.5	22	15	42	5.4
A10-I	66	0.3	0.006	1	3.3	0.04	0.02	26	0.3	12	7.7	43	10	22	17	49	6.8
A11-I	56	-	-	-	-	-	-	-	-	11	8.4	41	0.45	17	15	48	0.5
A12-I	53	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A12-II	53	-	-	-	-	-	-	-	-	0.8	1.1	55	0.32	1.1	1.8	73	0.9

TABLE 5 - PRIMARY EXPERIMENTAL DATA FOR THE BERYLLIA COATED FUEL PARTICLES

Run	Fuel Particles				Mass of Bed g.	Temperature of Bed °C	Reactant Conditions					Time of Run hours	Analysis of coated Particles % by wt. BeO	Particulates coated and recovered %	Material Balance on Fuel %	Conversion Efficiency %	Bed Efficiency %	Coating Thickness microns	Coating Rate		Comments
	Material	Lot No.	Density g/cc	Particle Size B.S.S.			Argon rate l/min at S.T.P.	BeCl ₂ rate g/min.	H ₂ O rate g/min.	BeCl ₂ /H ₂ O mole ratio	Average total pressure mm Hg								microns per hour	g/(hr) (g of bed)	
B1-I	(U,Th)O ₂	88	9.82	-72+100	50.1	1000	2.7	0.10	0.16	0.14	790	1.75	1.7	98.4	99.2	98	29	3	1.7	0.010	
B1-II					47.7	1000	2.1	0.79	0.14	1.27	810	1.5	7.2	99.3	99.8	45	13	11	7.3	0.042	
B2-I	(U,Th)O ₂	91,93	9.80	-72+100	50.0	1000	2.85	0.18	0.13	0.31	800	4.5	9.7	99.4	99.4	92	35	14	3.1	0.024	
B3-I	(U,Th)O ₂	94	9.94	-72+100	51.8	1000	2.95	0.20	0.10	0.45	800	5.0	12.8	100.0	100.4	93	40	14	2.8	0.029	
B4-I	(U,Th)O ₂	99,102	9.78	-72+100	48.2	1000	2.92	0.31	0.078	0.89	820	3.0	6.3	95.4	97.2	71	18	3	1	0.022	
B5-I	UO ₂	153	10.71	-72+100	51.6	1000	2.2	0.16	0.077	0.47	800	4.75	7.2	99.3	102.7	91	28	12	2.5	0.016	
B6-I	UO ₂	157,154	10.64	-72+100	50.4	1000	2.79	0.12	0.067	0.40	810	1.5	2.34	-	-	(82)	(36)	8	5.3	0.016	BeCl ₂ leak from apparatus
B7-I	UO ₂	160	10.76	-72+100	49.6	1000	2.96	0.25	0.081	0.69	810	6.0	10.6	88.3	90.0	88	19	16	2.7	0.020	
B8-I	U ₃	189,192	10.80	-72+100	50.1	1000	2.76	0.18	0.080	0.51	820	3.17	3.2	96.6	98.2	-	(15)	6	2.0	0.010	Equipment broke during run
B9-I	UO ₂	192	10.74	-72+100	49.9	1000	2.89	0.102	0.078	0.29	810	7.5	8.9	99.2	100.0	97	33	10	1.3	0.013	
B10-I	UO ₂	192	10.74	-72+100	49.9	1000	2.94	0.24	0.096	0.56	820	5.0	15.0	99.0	99.2	94	38	14	2.9	0.035	
B11-I	UO ₂	192	10.74	-72+100	50.0	1000	3.03	0.49	0.17	0.65	820	2.66	13.2	100.8	101.2	95	32	15	5.6	0.057	
B12-I	UO ₂	205	10.40	-72+100	49.4	1000	2.83	0.96	0.15	1.4	860	1.17	7.1	82.1	82.1	39	15	9	7.7	0.065	
B13-I	UO ₂	205	10.40	-72+100	49.8	1000	2.95	0.19	0.083	0.51	820	4.0	10.5	97.2	98.8	94	39	14	3.5	0.029	
B13-II					49.1	1000	2.89	0.28	0.078	0.81	800	4.5	24.1	96.5	97.1	62	36	30	3.6	0.040	
B13-III					50.3	1000	2.95	0.25	0.071	0.79	820	4.83	34.4	98.0	98.2	76	34	40	2.1	0.032	
B14-I	UO ₂	205	10.40	-72+100	51.4	1000	2.92	0.18	0.068	0.59	800	5.0	12.5	96.2	96.2	92	42	15	3.0	0.029	
B14-II					49.7	1000	2.92	0.187	0.077	0.55	810	5.0	22.1	97.8	98.0	91	34	26	2.2	0.025	
B14-III					50.0	1000	2.93	0.185	0.075	0.56	800	4.0	29.3	96.3	97.3	87	35	32	1.5	0.025	
B14-IV					49.8	1000	2.87	0.185	0.075	0.56	790	4.0	36.1	89.2	98.0	92	35	40	2.0	0.027	
B15-I	UO ₂	207,209	10.5	-72+100	49.9	1400	1.97	0.33	0.080	0.93	800	1.83	8.4	85.3	102.4	77	35	-	-	0.050	
B16-I	UO ₂	207,245	10.4	-72+100	50.0	1400	2.02	0.23	0.093	0.56	800	2.0	5.8	78.4	86.4	(64)	(29)	-	-	0.031	BeCl ₂ leak from apparatus
B17-I	UO ₂	292	10.42	-72+100	50.0	1400	3.4	0.23	0.088	0.59	800	2.5	11.5	-	-	57	-	27	11	0.052	
B18-I	UO ₂	292	10.42	-72+100	50.1	1400	3.5	0.30	0.073	0.74	810	5.5	39.4	-	-	78	-	41	7.4	0.10	
B19-I	(U,Th)O ₂	219	9.35	-72+100	50.4	1400	3.8	0.30	0.080	0.84	810	2.5	8.7	-	-	61	-	8	3.2	0.038	

TABLE 6
EVALUATION DATA FOR THE BERYLLIA COATED FUEL PARTICLES

Run	Knoop hardness kg/mm ²	Acid-leaching 1st 6 hours		Air Oxidation UO ₂ oxidised %	Chemical Analysis of Coating		U as sur- face con- tamina- tion (as produced) %
		U diss. %	Be diss. %		Si ppm	Cl ⁻ ppm	
B1-I	-	-	-	-	-	-	-
B1-II	280± 140	-	-	-	-	-	-
B2-I	850± 240	-	-	-	-	-	-
B3-I	1210± 220	-	-	-	-	-	-
B4-I	-	-	-	-	-	-	-
B5-I	-	6.0	17	~ 1	160,000	1600	0.08
B6-I	-	95	80	-	-	-	-
B7-I	980± 270	91	69	41	8,400	240	0.05
B8-I	1300± 150	-	-	-	-	-	-
B9-I	1050± 240	96	60	-	1,700	2900	-
B10-I	1340± 390	95	33	75	-	-	-
B11-I	1010± 190	93	62	68	-	-	-
B12-I	520± 150	-	-	-	-	-	-
B13-I	1480± 90	-	-	64	3,200	2000	0.5
B13-II	-	91	39	-	-	-	0.16
B13-III	1070± 120	57	29	15	5,100	320	0.26
B14-I	1270± 160	92	37	36	5,800	2500	0.19
B14-II	-	-	-	-	-	-	1.0
B14-III	-	39	43	-	-	-	0.5
B14-IV	1360± 80	40	25	50	1,800	< 70	0.5
B15-I	-	-	-	-	3,300	240	-
B16-I	-	-	-	-	5,700	-	-
B17-I	-	87	8.4	-	3,500	730	-
B18-I	1100± 190	3.2	3.5	-	-	-	-
B19-I	1190± 240	-	-	-	-	-	-

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