Zircaloy Hazards in Nuclear Fuel Reprocessing

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Zircaloy hazards associated with the shear/leach operation of oxide fuel reprocessing are discussed. The ways in which the hazards were identified are discussed along with the development of supporting safety arguments.

The undertaking of long, complex and expensive research and development work, and how this changed the arguments in the safety case, is described. The paper concludes by reviewing the current safety case, making observations on how problems were resolved as they arose.

1. INTRODUCTION

On the 26 September 1973 during the start up of the Oxide Fuel Reprocessing Plant at Windscale, a small quantity of acidified dibutyl carbitol (Butex) entered a vessel containing a hot bed of accumulated particulate solids. The solids comprised insoluble fission product particles and finely divided zircaloy. One or more exothermic reactions took place leading to the decomposition of the Butex and possible ignition of the zircaloy. The reactions resulted in pressurisation and the release of a small amount of radioactive ruthenium to the operating area. Detailed incident investigations were then undertaken by both BNFL and the Nuclear Installations Inspectorate.

The reactive nature of finely divided zircaloy was already well appreciated. Incidents involving zirconium and its alloys were happening in the late forties and fifties. When the first Oxide Reprocessing facility (known as the 'Head End Plant') was brought into operation at Windscale, research work had already examined the reactive nature of finely divided zircaloy in order to define safe operating conditions. As a result of the incident, the Oxide Fuel Reprocessing Plant was shut down. A white paper containing the Report of the Chief Inspector of Nuclear Installations was published in July 1974 (Ref 1). This paper made a number of recommendations, several of which related to plant modifications, to ensure that reactive solids would not be allowed to accumulate in potentially hazardous quantities.

When the proposals for a second Thermal Oxide Reprocessing Plant (THORP) were examined at the Windscale Inquiry of 1977, the potentially hazardous nature of finely divided zircaloy was raised as a specific issue in the BNFL proof of evidence (Ref 2). Zirconium and zircaloy were clearly going to be the subject of close attention in the safety arguments supporting the THORP project.

Nuclear power stations currently provide about 17% of the UK electricity demands and are presently of two types: the Magnox stations which utilise uranium metal fuel clad in a magnesium alloy, and the Advanced Gas-Cooled Reactor (AGR) stations which use uranium oxide fuel clad in stainless steel.

In other parts of the world a further type of nuclear reactor is widely used, the light water reactor (LWR). The construction of such a reactor in the UK is the subject of the Sizewell Inquiry. This reactor type utilises a uranium oxide fuel clad in zircaloy.

Only the UK and France presently provide a commercial scale reprocessing operation. Reprocessing began at the Sellafield site (formerly called Windscale) 30 years ago and since then about 28,000 tonnes of Magnox fuel and about 100 tonnes of oxide fuel from the UK and overseas has been reprocessed (of the 100 tonnes of oxide fuel reprocessed, about 70 tonnes was zircaloy clad). With the anticipated arising of up to 200 tonnes a year of oxide fuel from Home Board AGR stations the need for a new thermal oxide reprocessing facility became clear.

THORP is intended to reprocess AGR and LWR fuels and is due to start up in 1990. For the initial 10 year operation 6000 tonnes capacity is already taken up, about one third coming from the Home Boards, the remaining two thirds come from overseas. The total cost of the THORP project will be about £1,300 million (excluding the fuel receipt and storage facility and the associated waste treatment plants).

2. The Shear/Leach Operation in THORP

The THORP process has been described by Bennett (Ref 3). The shear/leach operation in THORP is shown in Fig 1. This involves chopping oxide fuel assemblies, some of which have zircaloy cladding, into lengths of between 2-10 cms, the sheared fuel then falls into a basket located in a dissolver containing nitric acid. Chopping also produces both fuel and cladding fines which are drawn into the dissolver by the air stream which passes through the shear machine. In the dissolver the fuel is dissolved leaving insoluble fission products (IFPs), cladding fines and the larger pieces of fuel cladding known as "hulls". The hulls, and a proportion of the fines, are retained in the basket which is removed and emptied after each dissolver batch. The remainder of the fines pass through the basket holes into the product liquor. These fines are removed in downstream plant by a combination of settling/decanting and centrifugation. The removal of the insoluble zircaloy and fission product fines at an early stage in the process means that this material will not pass into the solvent extraction stages downstream.

In THORP, zircaloy will arise in the following conditions:

i. A mixed zircaloy/fuel dust cloud in the vicinity of the shear and shear chute.

ii. A dry mixed layer of zircaloy fines and fuel dust in the shear machine, and on the shear chute.

iii. A mixed layer of zircaloy fines and insoluble fission products. These can occur as dry, moist, or submerged layers in vessels.

iv. Cladding hulls and fines in the dissolver basket.

N.B. Settled layers containing zircaloy fines fuel dust and IFP's are heat generating due to fission product decay.

3. The Identification of the Potential Hazards in the Plant due to the Presence of Zircaloy

The identificaton of potential hazards was effected in three ways; by literature review; by individual process assessment using qualified professionals, and by hazard and operability studies using experienced multi-disciplinary teams.

The literature review took two forms; a review of worldwide experience on the shear leach reprocessing of zircaloy clad fuel, and a review of fire/explosion incidents involving zirconium and its alloys in industry in general.

The first review concluded that the only reported incidents attributed to the presence of zircaloy, occurred at the West Valley Plant, USA, which operated from 1966 to 1972 (Ref 4). However these incidents occurred during the processing of zircaloy clad uranium metal fuel which will not be reprocessed in THORP. The review also concluded that no incidents, that could be attributed directly to zircaloy, had occurred during the reprocessing of zircaloy clad oxide fuel. By July 1980 in excess of 950 tonnes of zircaloy clad oxide fuel had been reprocessed by the shear/leach method.

The second review reinforced the view that under certain conditions zirconium and its alloys could indeed be a hazardous material as there have been in excess of forty incidents with this material since the late nineteen-forties, some with fatalities. Whilst it was not possible to obtain complete explanations for the majority of the incidents so many years after the event, none of the incidents reported in open literature took place in conditions similar to THORP.

What was clear from the reviews was that the oxidation of zirconium and its alloys could be violent, particularly where the configuration of the reactive metal and oxidising environment was such that heat removal was likely to be slow. The more finely divided the material, the greater its accumulation, the more effective the oxidising agent, etc., the greater the potential hazard.

The critical appraisal of the THORP shear/leach process by individual assessment and by the HAZOP teams, identified that there were several areas of concern with respect to zircaloy hazards which were:

i. Zircaloy dust explosions in the vicinity of the shear

ii. Ignition layers, dry or submerged

iii. Fire spreading from zircaloy fines in the dissolver basket to the hulls.

Item iii was shown not to pose a problem. Attempts to ignite hulls were shown to be unsuccessful in the literature (Ref 5). Additional work undertaken for BNFL also found that hulls could not be made to sustain ignition even when heated with an oxyacetylene torch.

The remainder of the paper addresses the development of the arguments for items i and ii.

4. The Development of the Safety Case for Zircaloy Dust Explosion

Work had been undertaken in 1964/1965 to examine the potential hazards of zirconium and its alloys for the first Oxide Reprocessing facility at Sellafield. In 1978 an internal BNFL paper was submitted to the THORP design committee which outlined the hazards and proposed additional research work at BNFL Springfields to examine in further detail the ignition behaviour of zircaloy with and without nitric acid, uranyl nitrate, and other process components. It also recommended the measurement of explosion limits for the system, the ignition behaviour of irradiated zircaloy, and the production of supplementary data for specific process operations. The initial estimate of the research effort required was 5 man years. Seven years on, the total research effort for this work is likely to be in excess of 50 man years.

Further reviews of the research work were undertaken in 1979 and in 1980. When in 1980 the safety arguments were re-examined it was noted that dust explosion hazards are often ranked for severity in terms of the maximum rate of pressure rise measured in the Hartmann apparatus. For zirconium dust this could be as high as 23,000 psi/sec, the most reactive dust tested by Wolfson Applied Electrostatics Advisory Unit where the work was being undertaken. Accepting that the dust was explosive, the approach in 1980 was to examine the design options available for dealing with a dust explosion. The early review concluded that in the chemical industry, there are three ways of dealing with dust explosion hazards viz:-

i. Contain the explosion
ii. Vent the explosion
iii. Inert the system.

i. Explosion containment

In order to contain the explosion, the process enclosure must be capable of withstanding the maximum explosion pressure.

A maximum figure for this pressure can be estimated from thermo-chemical considerations. Dust is known not to have generated a pressure above 150 psia, and for Zr powder 60-90 psi has been observed. (Ref 6). The maximum pressure will be observed at about 10% above stoichiometric concentration, and will not be affected by particle size, turbulence, or ignition source strength. Whether the shear cave can be engineered to this design parameter is open to debate, but it is considered unlikely. A second highly undesirable feature of this strategy is that dust explosion incidents are often two-stage. One effect of the primary explosion is to throw into the air any dust previously present as a dust layer on ledges and similar inaccessible places. A so-called secondary dust explosion then often follows, which is usually much more violent than the primary, due typically to a much larger fuel inventory and the high turbulence generated by the initiating event.

ii. Explosion Venting

The use of explosion vents (discs, explosion panels, dead weight relief valves and so on) is a well established technique in powder-handling plant in the process industries. Typical examples are flour mills and similar plants handling organic and pharmaceutical products. Such plant (silos, cyclones, filters, spray dryers etc) is usually very weak mechanically and a pressure rise of a few psi is normally sufficient to rupture it.

Leaving aside the difficult question of where a dust explosion could be vented to, there could still be some difficulty with the process design of such a protective system. Choice of design parameters (vent area, rupture pressure) is not an exact science. An obvious, but frequently overlooked point, is that the transient pressure inside an exploding vessel being relieved by a rupture disc will exceed, sometimes by a wide margin, the rating of the disc. The sizing of the disc is related to the measured rate of pressure rise and the main problem is related to the estimation of this parameter. Rates of pressure rise are known to be affected by dust concentration, particle size, turbulence and strength of ignition source. There is a well known relationship (see for example Ref 7) due to Bartknecht (the "cubic law") which says "that for a given dust and concentration the maximum rate of pressure rise is inversely proportional to cube root of the vessel volume". This can be used to scale to full size from test data. Unfortunately it can be shown that this relationship implies that the flame speeds in test vessel and plant are the same, which is extremely unlikely in practice, due to the profound effect of turbulence level. There is also a substantial body of opinion that holds that the Hartmann apparatus is too small for valid scaling of maximum rate of pressure rise.

It seems clear, even from this cursory examination that a credible safety case could not be assembled based on explosion relief.

iii. Explosion inerting

> There remains the question of inerting i.e. to what level must the oxygen concentration be reduced to render the dust cloud non-flammable. This limiting oxygen concentration was measured by Hartmann (ref 6) as 4% in argon and nitrogen and slightly higher for helium. As the metal will burn in carbon dioxide, this gas is ineffective. It supports the contention that inerting with nitrogen would be adequate, despite the possible reaction with the metal at high temperatures. The size-related objections to the Hartmann apparatus, referred to above, in connection with rates of pressure rise, do not apply to observations of critical oxygen concentration: similarly it is not greatly affected by turbulence, ignition source strength (within reason) nor by particle size.
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> Thus it appears that gas inerting is a technically feasible way of ensuring safe working conditions during shearing. It shares with "containment" the advantage that it depends upon parameters which are easy to establish, and are not affected by such vagaries as local turbulence levels etc".

The review went on to discount the possibility of thermite-type reaction between zircaloy and fuel dust because of the unfavourable thermodynamics, and noted that the presence of fuel dust in certain proportions could effectively act as an inertant for the dust explosion. Demonstrating that fuel dust also generated during shearing would effectively inert the dust cloud was, the review suggested, the most attractive option, though inert gas, which was employed on most other shear/leach reprocessing operations, was a clear fall back position.

Further reviews of the safety case arguments were undertaken in 1981 and 1982. By this time a substantial research and development programme was underway at the Wolfson Applied Electrostatics Advisory Unit and the parameters of interest were now clear. The work was aimed at defining the minimum explosive concentration (MEC), the minimum ignition energy (MIE), the maximum explosion pressure (MEP) and the maximum rate of pressure rise (MRPR) for zircaloy dust clouds of various narrow size range particles down to 5 micron and clouds of mixed sized particles. The effect of uranium dioxide as an inertant was also examined.

The concentration of zircaloy particles in the dust cloud is a function of the amount of dust generated during shearing, and information on this was available from the operation of the first Oxide Fuel Reprocessing Plant, and from work done at Oak Ridge in the US (Ref 8). However this data base was not sufficient in itself to give the safety assessors sufficient confidence that worst case fines generation rate could be predicted. Further work was clearly needed to examine the effect on fines generation of such parameters as, degree of hydriding (increased brittleness), work hardening of pins, (which simulates neutron damage) and deterioration of shear blade.

By 1980 it was becoming clear that an argument could be assembled to demonstrate the safety of normal operating conditions in the shear machine. The argument would be based on a low average zircaloy dust concentration in the cloud and the presence of fuel dust acting as an effective inertant. The alternative of inerting the shear and its associated ductwork was not seen as either attractive or practicable. This was mainly because of the realisation that to inert the whole shear, given the ventilation flows required to maintain a depression on the equipment, would require very substantial quantities of the inertant. In addition, since the oxide film attached to the zircaloy particles slows the oxidation of zircaloy very considerably, and because the use of a nitrogen inertant might prevent an oxide layer forming, the potential hazards in process downsteam of the shear could become more severe.

The latest progress statement on the safety case for zircaloy dust cloud hazards is able to be more positive about the safety of both normal and fault conditions in the THORP shear machine.

BNFL has obtained results from its programme of shearing trials which show that the worst case mass arisings of fines are similar to those reported by the ORNL workers (Ref 8) though the particle size distribution is seen to be lower in fine material (see Figure 2). The average concentration of fines in air in the region of the shear has been estimated to be thirty times less than the MEC measured at Wolfson. Of course, as the dust cloud expands from the point of generation into the air, it will pass through the flammable region. Again calculations show that the ignition of this small portion of the dust cloud in the flammable envelope is of negligible consequence. Also from the Wolfson work, the amount of uranium dioxide needed to effectively inert the cloud, is seen to be less than one third of that expected to be present in the process at this point. Due to the time taken for particles to settle, even if all air flow though the shear is lost it can be shown that sufficient UO_2 remains in suspension to ensure that the cloud is effectively inerted at all times. (Figure 3)

It has also been shown that under the worst foreseeable fault conditions (total shear air loss and continued shearing) sufficient fines cannot be held in suspension to reach the MEC and as previously stated, the cloud remains effectively inerted by the UO_2.

The research and development work has enabled a strong case to be made that a zircaloy dust explosion will not occur in the shear. Thus the safety case is not dependant on analysis of risk using probabilistic assessment and detailed consequence analysis. Neither is it dependent on demonstrating the adequacy of an engineered shear inerting system. The extensive research and development costs can be seen to be a wise investment when considered against what would have been considerably greater capital and operating costs of an inerting provision with a possible deterioration in downstream process safety.

5. The Development of the Safety Case for Layer Ignitions

Since the early incidents involving zirconium and its alloys, it has been realised that finely divided material, particularly in the moist state was reactive. However when BNFL undertook experimental work in 1965 in support of the first Oxide Reprocessing Plant operation, an explosion was seen when attempts were made to ignite particulate zircaloy under boiling 12M nitric acid. This was not observed in 6M acid. On the basis of this work the first plant was operated using acid concentrations of 6M or less.

In later experimental work, undertaken at Springfields, BNFL provided evidence that particulate zircaloy could apparently explode or react vigorously in 6M nitric acid. Clearly, before THORP processes could be shown to be safe in this respect, further investigation was necessary.

It was known that a passivating oxide layer formed on the particles of zircaloy. While the oxidation reaction did not completely cease, it slowed markedly when the oxide layer was present.

The earliest thoughts on the demonstration of THORP process safety centred on an understanding of the reaction kinetics and thermodynamics, combined with the heat transfer characteristics of the particular settled layer configuration. In this way it was thought that a critical bed thickness could be determined for any areas or vessels where solids might settle out. The investigation of submerged layer ignitions is now discussed in more detail to provide an example of the way in which the work was undertaken. In the THORP process solids can settle in most vessels in the Head End Section of the plant. In a number of cases this is by design, while in others layers can form due to maloperation or other fault conditions.

With the general approach having been identified work proceeded in three ways:

i. Experimental investigation of the reaction kinetics

ii. Empirical experimental work to reproduce conditions under which a thermal runaway could be seen. This enables a safe region to be identified.

iii. Development of a mathematical model of the settled layer heat transfer characteristics.

In the years since 1978, in excess of 35 man years resource has been applied to this problem in these three areas. Now, in 1985, it is considered that the level of understanding of this system is adequate for the demonstration of THORP process safety. The reaction of zirconium and its alloys with nitric acid of all molarities, in the absence of a passivating oxide film, is extremely fast, to the extent that experimental techniques have been seen in some cases to be inadequate or pushed to the boundaries of their applicability.

However, this fast reaction simultaneously generates the protective oxide film and in no case has an unstable, non-repairing situation been observed when studying the system for normal and foreseeable maloperation process condition for THORP.

The kinetic investigation has combined electrochemical and thermal analysis techniques. The electrochemical technique employed in the early 1980's involved scanning the voltage from an abraded zircaloy electrode at low temperature (50°C) while at high temperatures (up to a 100°C) a microsecond switching technique was required. From the former, both anodic and cathodic curves could be plotted on the corrosion current/emf plot, while for the latter only the anodic curve could be constructed. Using Tafel theory (Ref 9) an attempt was made to determine the exchange current density. Repeating the experiment at different temperatures enabled an Arrhenius plot to be constructed and the kinetic parameters to be predicted. However it became apparent that the reaction was so fast that oxide product filming was interfering with the results making the kinetic parameters predicted those for partially filmed zircaloy and not the "bare" metal. Alternative techniques were sought and in recent years the following techniques have been employed with success:

a. Slow scan potentio-static sweep and galvanostatic experiments (Ref 10)

b. AC impedance experiments (Ref 11)

c. Scratched disc transient experiments (Ref 12)

d. Differential Scanning Calorimetry (DSC)

e. Differential Thermal Analysis (DTA)

f. Raman Spectroscopy

The first two techniques examined the stability of the protective oxide film, while the third technique sought to deduce the "bare" metal kinetic parameters. The fourth and fifth are classical thermal analysis techniques which brought some diversity in the experimental methods used to examine the system (nearly all the other techniques were electrochemical in nature). The sixth technique was used to examine the nature of the oxide film.

Resulting from this work, was an understanding of the conditions under which the protective oxide film is stable, a realisation of the extreme speed of the "bare metal" oxidation reaction (corrosion currents of a 1000 amps/cm^2), and hence the importance of ensuring that conditions conducive to the presence of a stable oxide film should be employed.

The techniques referred to in items a and b have been used to show the regions of stability of the oxide film and to confirm that THORP process conditions are such that one would not conceive of loss of the protective oxide film leading to rapid exothermic reactions. The rate of reaction with the protective film is small and the DSC and DTA work confirms that a very low heat output is obtained from the zircaloy reaction in THORP process conditions.

The empirical work examining layer ignitions has progressed in the period 1980 to 1985, after overcoming many experimental problems to enable the reproducible ignition from a point source of beds of zircaloy/zirconium particles submerged in nitric acid. Point ignition temperatures of less than 300°C have not been seen for any beds except where the thermocouple was subsequently discovered to be too far from the point ignition source. The effectiveness of insoluble fission products as an inertant has also been investigated, along with the possibility of thermite reactions between these materials and the zircaloy. It is now thought unlikely that thermite reactions will pose a problem; though the value of these materials as an inertant (or indeed any other inertant) for a bed that is heated throughout by decay heat is dubious.

The modelling work started by examining the use of the Frank-Kamenetskii model for slab and cylindical bed geometry (Ref 13). Later, a classical transient heat conduction model with a suitable semi-empirical reaction term was developed. However it became clear that the heat of reaction from zircaloy oxidation was relatively small while the conditions favoured a stable oxide film. A simpler conduction model was developed which included a fixed heat input from decay heat and the zircaloy heat of reaction.

Notwithstanding the model development the main arguments in the safety case centre on the adoption of THORP process conditions in which a protective stable zirconium oxide film is present. The models used are to show that the ignition temperature is not reached in a settled layer. The risk arising from plant faults leading to unsafe conditions resulting in a fire/explosion will also be quantified.

For a number of years it has been realised that the radiological risk arising from a zircaloy fire would be small, because of either the inventory of zircaloy or the plant containment standards adopted. However the occurrence of such an incident would imply an unacceptable loss of control in an industry which is under close media and public scrutiny. On this basis alone the considerable resources channelled towards the behaviour of zircaloy in nitric acid can be justified.

6. Discussion

Many of the techniques adopted in this investigation are applicable to other reactive metal systems. The reactions of zirconium are extremely fast unless the metal surface is passivated and as such, it is a system that has provided a challenging problem in finding experimental techniques capable of dealing with it. The lessons learnt during the study are of value to future workers in the field. With the advent of the Control of Major Hazards (CIMAH) Regulations, the Chemical Industry will have to prepare safety cases. The Nuclear Industry has had to do this for many years. The detail that such cases contain will probably continue to be greater in the Nuclear Industry compared to the Chemical Industry for some time to come. Nevertheless all companies need to convince themselves that their processes are safe, particularly in the aftermath of major incidents such as Mexico City and Bhopal.

In this paper an example has been presented of the significant amount of time and resources that may need to be committed to a single aspect of a process. It is clear that after more than twenty years of investigation into zircaloy related hazards in BNFL (and continuous involvement over the last seven years) the arguments demonstrating process safety have changed. The value of undertaking such investigative work would be irrefutable if measured against the loss to the Nuclear Reprocessing Industry arising from a serious zircaloy related fire or explosion. The cost of lost production and modifications to plant and processes would be small compared to the implications of the loss of public confidence, and an increased antipathy towards nuclear power.

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Fig 1. Thorp Head-End Plant Process Scheme

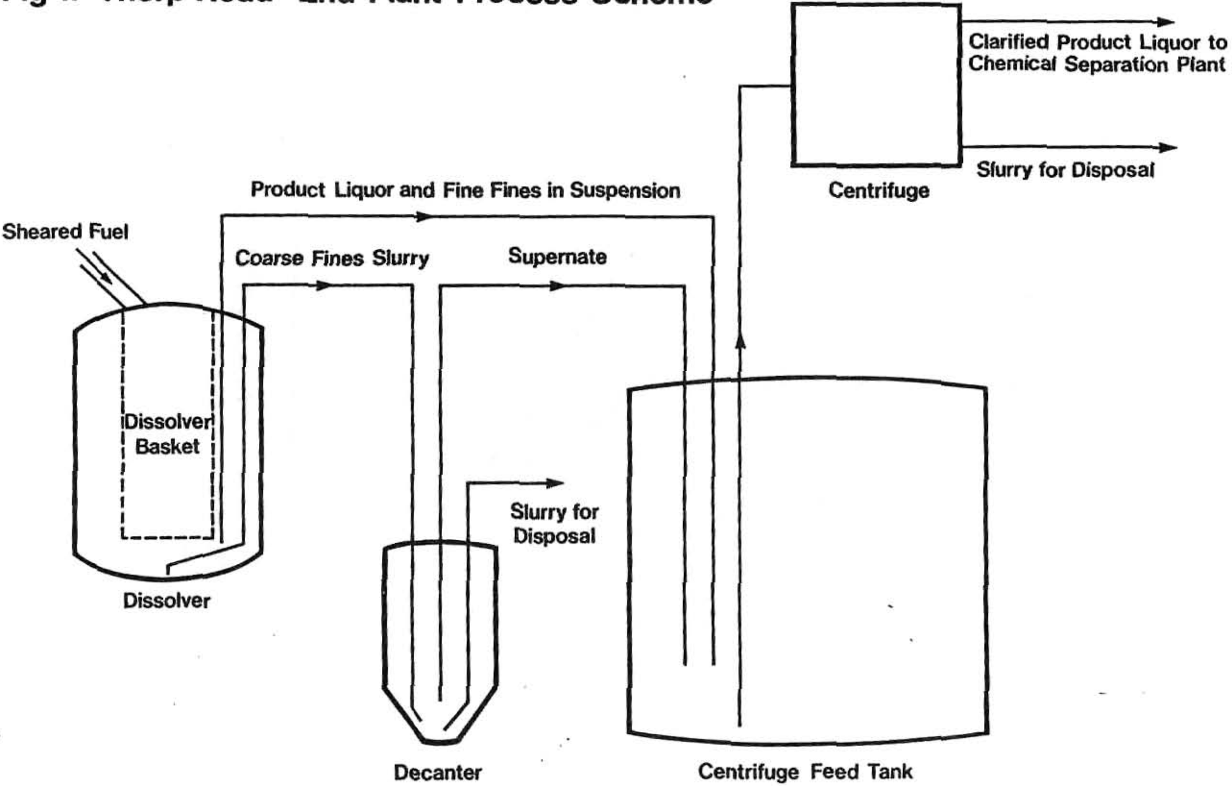
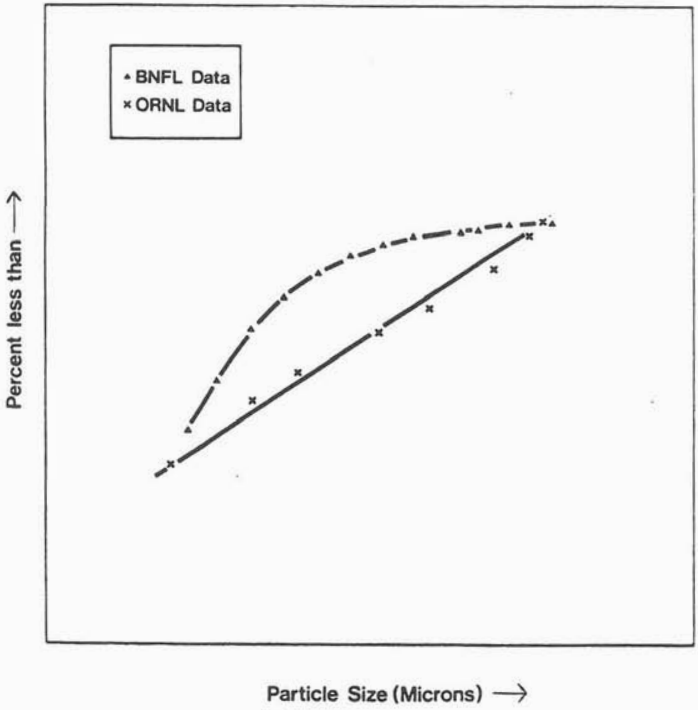


Fig 2. Size Distribution for Sheared Zircaloy



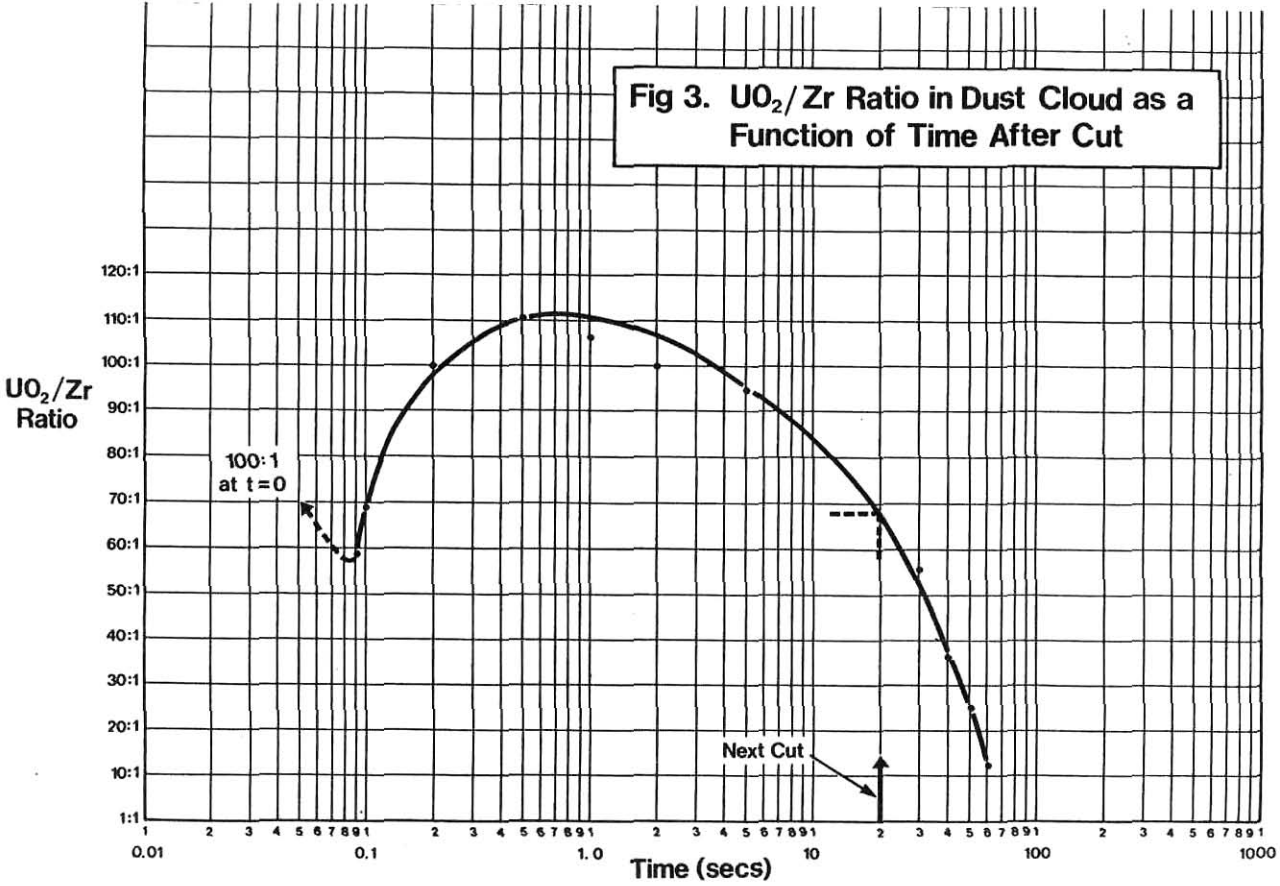


Fig 3. UO_2/Zr Ratio in Dust Cloud as a Function of Time After Cut