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Treatment of zircaloy cladding hulls by isostatic pressing

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ABSTRACT

A method for the treatment of Zircaloy fuel hulls is proposed. It involves hot isostatic pressing (HIP) for making large, completely densified metallic bodies of the waste. The hulls are packed into a bellows-shaped container of steel. On packing the fuel hulls give a filling factor of only 14 %, which is too low for non-deformable compaction in a normal container, but by using a bellows-shaped container, a non-deformable compaction can be obtained without any pretreatment of the hulls. Fully dense and mechanically strong blocks of Zircaloy can be fabricated by holding them at temperatures of around 1000 °C for three hours.

It is also feasible to incorporate the other metallic parts of of the fuel bundle, such as top and bottom tie plates and spacers, in the pressing.

The HIP-densified hulls provide an effective means of self-containment of radioactive waste due to the excellent corrosion resistance of Zircaloy. A waste loading factor of close to 100 % can be realized. Further, a volume reduction factor of 7 and a surface reduction factor of about 250 for a 1-ton canister can be achieved.

Equilibrium calculations have shown that tritium present in the hulls can quantitatively be contained in the HIPed block.

A study has been made of a possible process for industrial-scale use.

1. INTRODUCTION

Spent fuel and certain other components from nuclear power plants contain large amounts of long lived radionuclides, which decay by emission of alpha, beta or gamma radiation in one or more stages to stable nuclides.

Since the exposure of living species to radiation represents a health risk, one of the major problems arising from the use of nuclear energy is the disposal of the resultant radioactive wastes. At present it is believed that the risk is linearly dependent on the radiation dose down to the zero level, which means that the only useful principle for limiting the global radiation hazard from radioactive wastes is containment and isolation. In some cases, long-lived nuclides must be segregated from the biosphere for millions of years.

In 1976, the Nuclear Fuel Safety project (The KBS Project) was started by the nuclear power utilities in Sweden. The KBS Project stimulated research and development in the nuclear waste field (1). At the same time, ASEA proposed the use of hot isostatic presssing (HIP) to fabricate dense blocks of a wide range of radioactive waste products (2). The HIP compaction process is especially promising as it requires only a few processing steps, permits virtually no release of dust or fumes and yields an almost maximally dense product at a reasonable processing temperature (3). Against this background it was quite natural that ASEA started a development program for the containment of nuclear wastes using HIP (3,4,5).

This study presents a process for the containment of reprocessed Zircaloy cladding hulls mixed with fuel element parts such as endplates and spacers. The low fill density of untreated hulls required a bellows canister design, which is axially resilient. The stainless steel bellows canister, filled with Zircaloy fuel hulls, can be hot isostatically pressed and densified to a homogeneous corrosion-resistant material ready for final disposal. The process is successfully demonstrated with simulated hulls in a 15- litre canister. Metallurgical interactions during HIP between Zircaloy and common structural components in the fuel are discussed. The release and confinement of tritium in Zircaloy is also investigated.

2. CHARACTERISTICS OF CLADDING HULLS

Most commercial nuclear fuel is in the form of UO_2 pellets and is clad in thin-walled metal tubes. Two types of cladding are in common use: Zircaloy is used in water moderated reactors and stainless steel in gas cooled and liquid metal cooled reactors. Prior to reprocessing of the irradiated fuels to recover unused plutonium and uranium, the fuel elements are chopped into lengths of a few centimeters after a cooling period. Then the irradiated UO_2 fuel is leached from the cladding, usually with

a solution of nitric acid, leaving the leached hulls together with insoluble fuel residues.

The radioactive contents of the Zircaloy hulls originate from neutron activation of Zr and impurities in the cladding, as well as from contamination by fission products and actinides from the fuel. Contamination arises by several routes, the most important being tapered and undissolved fuel, embedded recoil atoms and nuclides that have diffused into the cladding from the fuel during irradiation. The limited data from the literature indicate that about 0.1-0.5 % of the fuel remains in the hulls or as an insoluble residue after the leaching operation (6). Results from Battelle show that most of the long lived alpha activity content is located on the inside surface of the hulls (7). The actinide content of the hulls is around 0.1-0.5 % of the total amount in the spent fuel. For Pu, this is roughly the same as in solidified high-level wastes. The amount of Zircaloy hulls depends on the fuel element design. For BWR fuel it is about 300 kg/ton* of uranium reprocessed (8). The hulls occupy an unconsolidated volume of about 0.35 m^3/ton of uranium, which is several times greater than the corresponding volume of the solidified high-level waste. A large future waste volume is therefore anticipated. It is probable that some form of volume reduction before final disposal will be advantageous for an efficient management of these wastes.

Given the actinide content of the hulls, they will have to be confined in a manner similar to high-level waste in order to prevent release of actinides to the biosphere. As untreated hulls represent a fire hazard with possible release consequences, whereas massive Zircaloy is resistent to ignition as well as highly resistant to corrosion, procedures for compaction and containment of hulls are considered necessary and economically advantageous.

3. ISOSTATIC COMPACTION TECHNIQUES

Hot isostatic pressing (HIP) is a process whereby an encapsulated powder mass is compacted into a fully dense body at temperatures below the melting point. Powdered materials or lumps of desired composition are packed into a flexible container of arbitrary shape. The container is usually made of sheet metal. After filling, the container is evacuted and sealed. During HIP, the powder body is subjected to high pressure and high temperature for a period 0.5 to 5 hours. The press consists of a pressure vessel with axially moveable end closures. The closures are supported by an external press frame. A furnace with thermal insulation, which shall operate at high temperature and high gas pressure, is placed inside the pressure vessel. The pressure medium normally an inert gas is pumped into the vessel, see Fig 1. The pressure is applied to the body by means of compressed gas. The gas acts perpendicular to all outer surfaces of the container and isotropically

* ton = metric ton (1000 kg)

squeezes the powder body. Since the pressure applied is relatively high, normally 50-300 MPa, most materials can be compacted to virtually pore-free bodies at only 50-70 % of their absolute melting temperature (9).

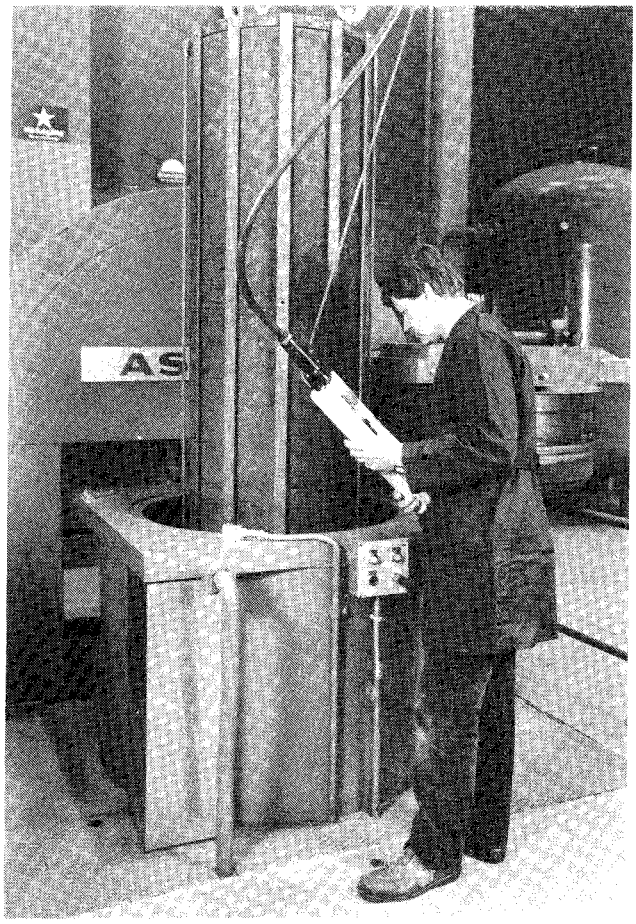


Fig 1. A hot isostatic press of ASEA QUINTUS® design during charging.

The HIP process has advantages compared with conventional sintering or melting in that undesirable grain growth and reactions between different phases or with the container envelope can be minimized, since a much lower process temperature is used. Further, compaction is performed with the product confined in a gas-tight container, preventing the release of dust or fumes.

Cold isostatic pressing (CIP) is a process whereby powdered material or lumps encapsulated in a pressure-tight envelope are compacted. CIP is performed at room temperature in a pressure vessel at a pressure of about 200-300 MPa. Oil or water emulsion is normally used as the pressure medium, but gas can also be used. The density obtained of the compacted material is normally 60-80 % of the theoretical maximum. The advantage of CIP is reduced size of the canisters and consequently of the HIP unit when CIP can be used as a pretreatment prior to treatment in a HIP unit.

4. HIP PARAMETER EVALUATION FOR ZIRCALOY

The Zircaloy hulls used in this study were made from tubes of Zircaloy II normally used for encapsulation of BWR fuel. The tubes had a diameter of 11.7 mm and a wall thickness of 0.8 mm and were delivered black-oxidized as for normal fuel preparation. The tubes were cut into 25 mm long pieces by a cutting wheel and then degreased and washed in water.

The HIP canisters used were made from low carbon steel or pure titanium tubes with an inside diameter of 80-85 mm, an inside height of 80 mm and a wall thickness of 3-5 mm. Pressure-turned lids were welded to the ends of the tubes. In this test series, only standard HIP canisters were used, as the main purpose was to find the most suitable HIP temperature and not an ideal canister design.

A canister filled with hulls has a filling factor of only 12-14 %, which is much too low for a non-deformable compaction by HIP. Therefore, the hulls were first flattened in a press to a mean thickness of 2.3 mm. Filling of flat hulls gives a fill factor of about 35 %, which is still a bit low for a non-deformable compaction. Filling of the hulls was therefore further improved by ramming by means of a cylindrical punch under a load of about 100 MN/m^2. After filling, the top lid with its evacuation pipe was welded to the canister. All canisters were then evacuated for 12-14 hours at a temperature of 150 ^{o}C, after which the pipes were welded vacuum-tight. then the pipes were welded vacuum tight.

Based on earlier HIP tests on hulls as well as HIP experience from other metals, the HIP parameters for pressure and holding time were set to 150 MPa and 3 hours, respectively. The HIP temperature was varied in steps of 50 ^{o}C from 900 ^{o}C to 1250 ^{o}C in a search for the most suitable temperature. During HIP, the heating rate was set to 400 $^{o}C/h$ and the cooling rate to 300 $^{o}C/h$.

Table I shows the canister material and HIP temperatures used. Density and strength values of the hulls after HIP are also given.

The minimum HIP temperature required to obtain a strong and fully dense body, ρ = 6.54 kg/dm^3, of Zircaloy hulls was 950 ^{o}C.

At a temperature of 900 ^{o}C, the density level drops to 4.7 kg/dm^3, which corresponds to a porosity of 27 %. Fig 2 gives the density of the HIPed hulls in the temperature range studied.

The strength of the HIPed hulls was measured by a conventional three point bending test. A small size of the test bars, 5 x 5 x 40 mm, was used as the main object of the test was to measure the bonding strength between different hulls and not the strength within a single Zircaloy hull. The strength values are given in Fig 3. Hulls HIPed at temperatures of 1000 ^{o}C or lower have a slightly lower strength and the fracture surface mainly follows the border between different hulls. The elongation of the HIPed hulls was 2-6 %.

Table I. Process and property data of Zircaloy hulls compacted by HIP at 150 MPa pressure for 3 hours at indicated temperature.

Canister type	HIP temp (^{o}C)	Density kg/dm^3	Strength MPa
Ti	900	4.74	0-100
Ti	950	6.54	720
Ti	1000	6.54	820
Fe	1000	6.54	700
Fe	1050	6.54	860
Fe	1100	6.54	1040
Ti	1150	6.54	1000
Ti	1200	6.54	1020
Ti	1250	6.54	950

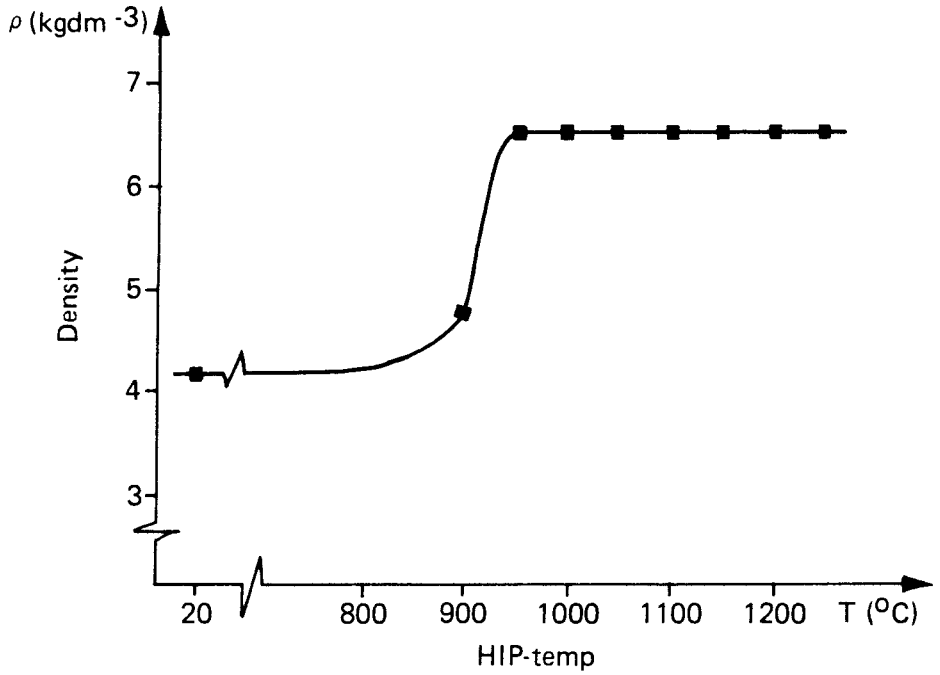


Fig. 2. Density of compacted Zircaloy II tubes with no additives. HIPed at 150 Mpa for 3 hours at indicated temperature.

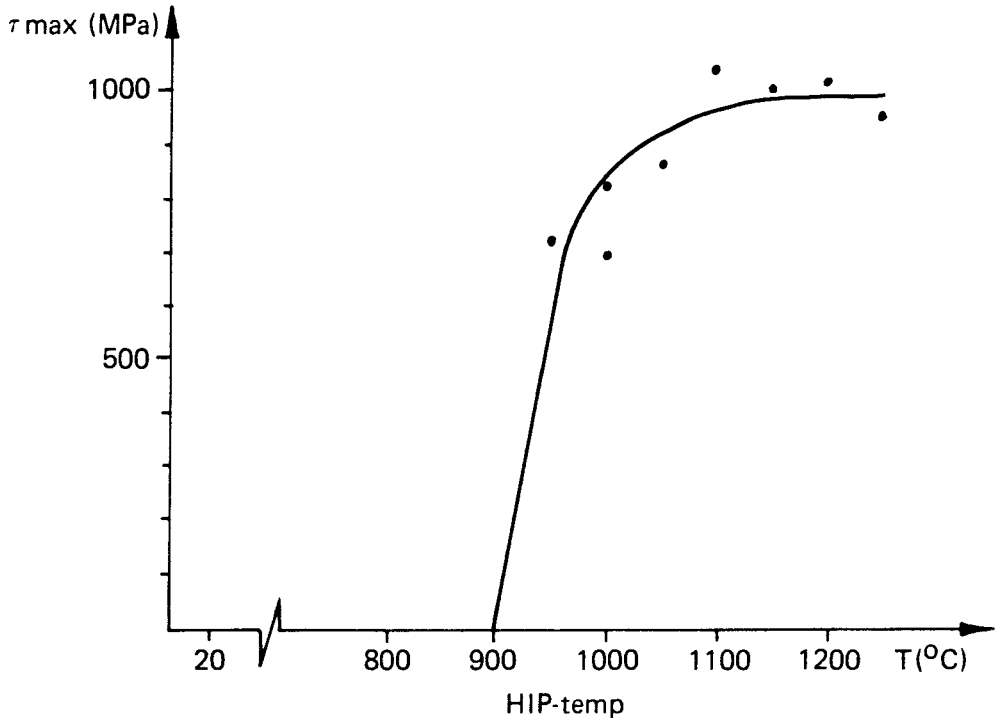


Fig. 3. Strength in 3-point bending of compacted Zircaloy II tubes with no additives. HIPed at 150 MPa for 3 hours at indicated temperature.

The microstructure of the joints between separate Zircaloy hulls HIPed at different temperatures is shown in Fig. 4. The HIP parameters are 950 ^{o}C, 1000 ^{o}C, 1050 ^{o}C and 1150 ^{o}C with a holding time of 3 hours at a pressure at 150 MPa. At a HIP temperature of 950 ^{o}C the joints between the hulls are very smooth and straight, but at 1000 ^{o}C a recrystallisation has started and a secondary grain can be observed in the joints. At the higher temperatures, considerable grain growth occurs and the joints are not easy to follow.

At a HIP temperature of 1100 ^{o}C or higher, the Zircaloy reacts with the Fe canister and forms a thick intermediate layer of Fe_2Zr and $FeZr_2$ phases. It is not recommended to use Fe canisters at temperatures above 1100 ^{o}C as canister damage caused by an excessive reaction with Zircaloy can occur. At a temperature above 1100 ^{o}C a peritectic melting of a η -phase occurs, giving a large amount of a liquid phase. Canisters made of titanium cause no problem at high HIP temperatures as no liquid phase occurs at temperatures below 1515 ^{o}C in the Zr-Ti system.

The present results concerning density, strength and morphology show that Zircaloy hulls can be HIPed to dense and strong blocks at temperatures of around 1000 ^{o}C in Fe or Ti containers at a pressure of 150 MPa for a holding time of 3 hours.

5. INFLUENCE OF OXIDE LAYER ON HULLS ON THE COMPACTED ZIRCALOY

The surface of the Zircaloy hulls has a black oxide layer with a thickness of 0.5-2 μm. The oxide layer on Zircaloy is intentionally formed, mainly by pretreatment in hot water vapour, in order to improve the corrosion resistance of the fuel cladding before use in the reactor core.

During HIP, the oxide layer is initially a barrier that prevents the formation of metallic bonds between the hulls, but at a HIP temperature of about 1000 ^{o}C, oxygen solubility in Zr is high (10). Further the diffusion of oxygen in Zr as well as in the different Zr oxides is high (11), and therefore metallic bonding can rapidly be obtained. HIP experiments at a temperature of 900 ^{o}C give only partial densification, but on the other hand the black oxide layers on the hulls disappear and metallic bonds are formed at contact areas between hulls. In another HIP experiment, black-oxidized hulls and ZrO_2 slices were mixed and HIPed at 1050 ^{o}C for 3 hours. At the ZrO_2 -Zr interface, the oxygen diffused about 250 μm into the Zircaloy as measured by increased hardness in the Zircaloy due to solid hardening. In normal contact areas between black-oxidized hulls, the corresponding diffusion zone with increased hardness is only 60 μm thick. The hardness of Zirconium increases rapidly with increased oxygen content. In this experiment the hardness and the oxygen diffusion in Zircaloy were visualized by lack of scratches in the contact areas of the rough polished samples (see Fig. 5).These two experiments

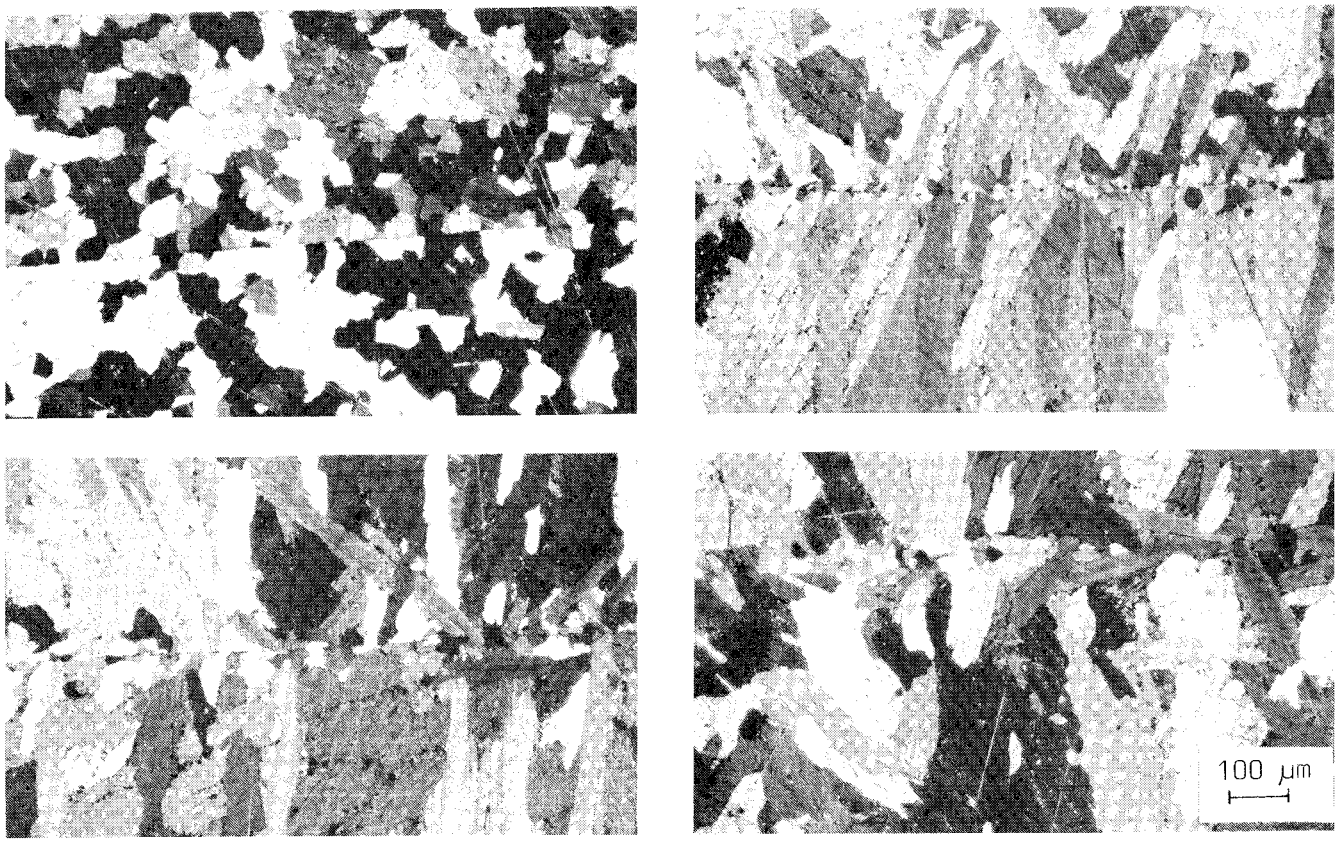


Fig. 4. Microstructure and joint in HIPed Zircaloy hulls, processed at 150 MPa and 3 h at 950 °C (top left), 1000 °C, (top right), 1050 °C (bottom left), and 1150 °C (bottom right).

Fig. 5. Interaction between Zirconia (left) and Zircaloy. HIPed at 1050 ^{o}C for 3 hours. Oxygen has diffused about 250 μm into the Zircaloy and increased its hardness (no scratches). Magnification 50x.
Oxygen from black oxidized hulls has diffused about 60 μm.

show that the reaction rate for oxide dissolution is sufficiently fast and is not a limiting factor for HIP of hulls.

The penetration depth of oxygen can be calculated from data on oxygen diffusion in zirconium (11). At a temperature of 1050 °C and a holding time of 3 hours, the calculated penetration depth is 200 μm, which is in good agreement with the experimental result.

6. INTERACTION BETWEEN ZIRCALOY AND STRUCTURAL COMPONENTS

In a reprocessing plant using the "chop and leach" process, the main stream of metallic waste is the chopped Zircaloy hull, but relatively large volumes of stainless steel and Inconel are also obtained from the dismantling of top and bottom tie plates and spacers from fuel bundles. An interesting option, which seems fully feasible, is to mix hulls with cut pieces of tie plates and spacers and HIP all the metallic waste forms in one single step. At a HIP temperature of 1000 °C or higher, Zircaloy reacts with both stainless steel and Inconel, forming a number of intermetallic phases. The corrosion resistance of HIPed Zircaloy might be reduced if the reaction with various metallic additives is too extensive. The extent of the reaction during HIP should therefore be minimized. Further, the materials used in the canister may react with the hulls or other additives and cause canister damage during HIP. Such events must be prevented.

The degree of reaction between Zircaloy, stainless steel and Inconel was therefore studied under realistic HIP conditions. The microstructure of formed phases was studied by SEM and composition was analysed by X-ray spectrography. The degree of reaction as well as the composition of formed phase can be explained with the aid of phase diagrams.

6.1 Interaction between Zircaloy and stainless steel

When Zircaloy hulls are HIPed together with stainless steel at a temperature of 1050 °C for 3 hours a 0.8 mm thick reaction zone is formed. Fig. 6 shows, from left to right, pure Zircaloy, a thick multiple phase zone rich in Zr, a thin zone rich in Fe and Cr and, finally, unreacted stainless steel. The microstructure analysis indicates that melting has occurred at 1050 °C. This is also in agreement with the binary Zr-Fe phase diagram (12), where a eutectic composition melting at 948 °C can be found. The reaction zone at the left consists mainly of three different phases. The X-ray emission analysis shows that Zr, FeZr and (Fe, Cr) Zr phase are present with some Ni in solid solution. The thin zone (50 μm wide) close to the stainless steel is rich in Cr and Fe and consists mainly of a $(Fe,Cr)_2$ Zr phase. This phase is probably an efficient diffusion barrier and prevents a rapid dissolution of stainless steel in Zircaloy. It can be seen from the two binary phase

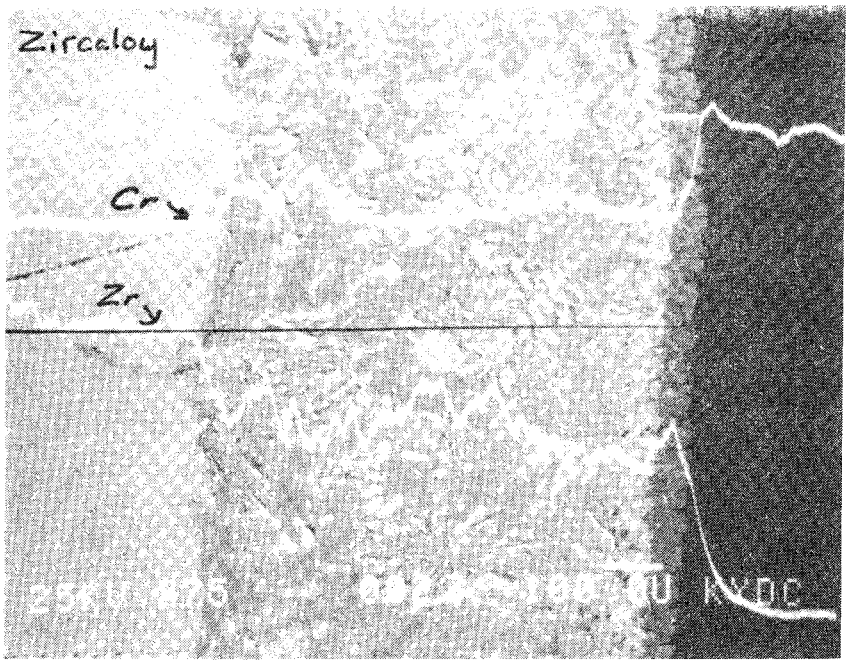


Fig. 6 a). Line analysis of Cr and Zr in interaction zone between Zircaloy (left) and stainless steel (dark zone, right).

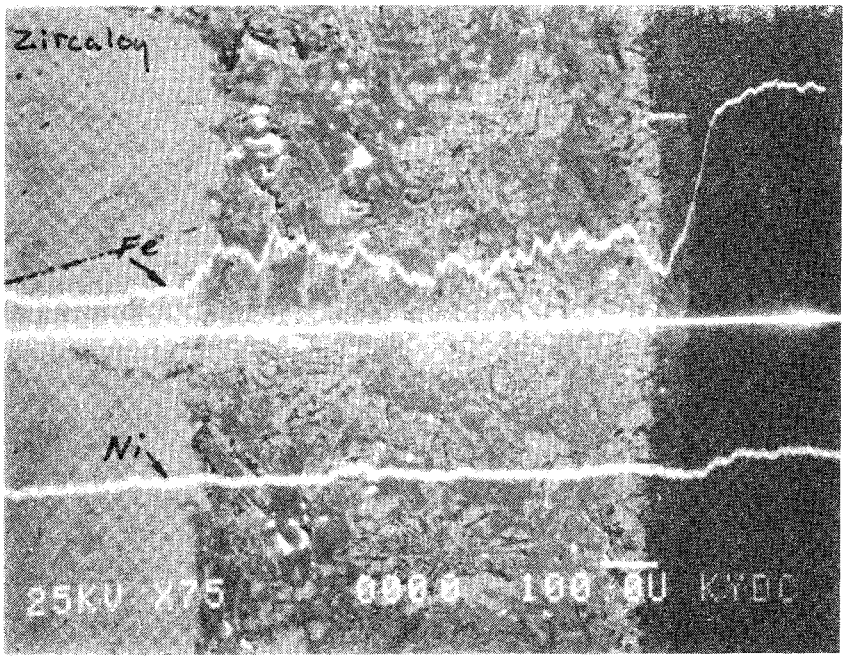


Fig. 6 b). Line analysis of Fe and Ni in interaction zone between Zircaloy (left) and stainless steel (dark zone, right).

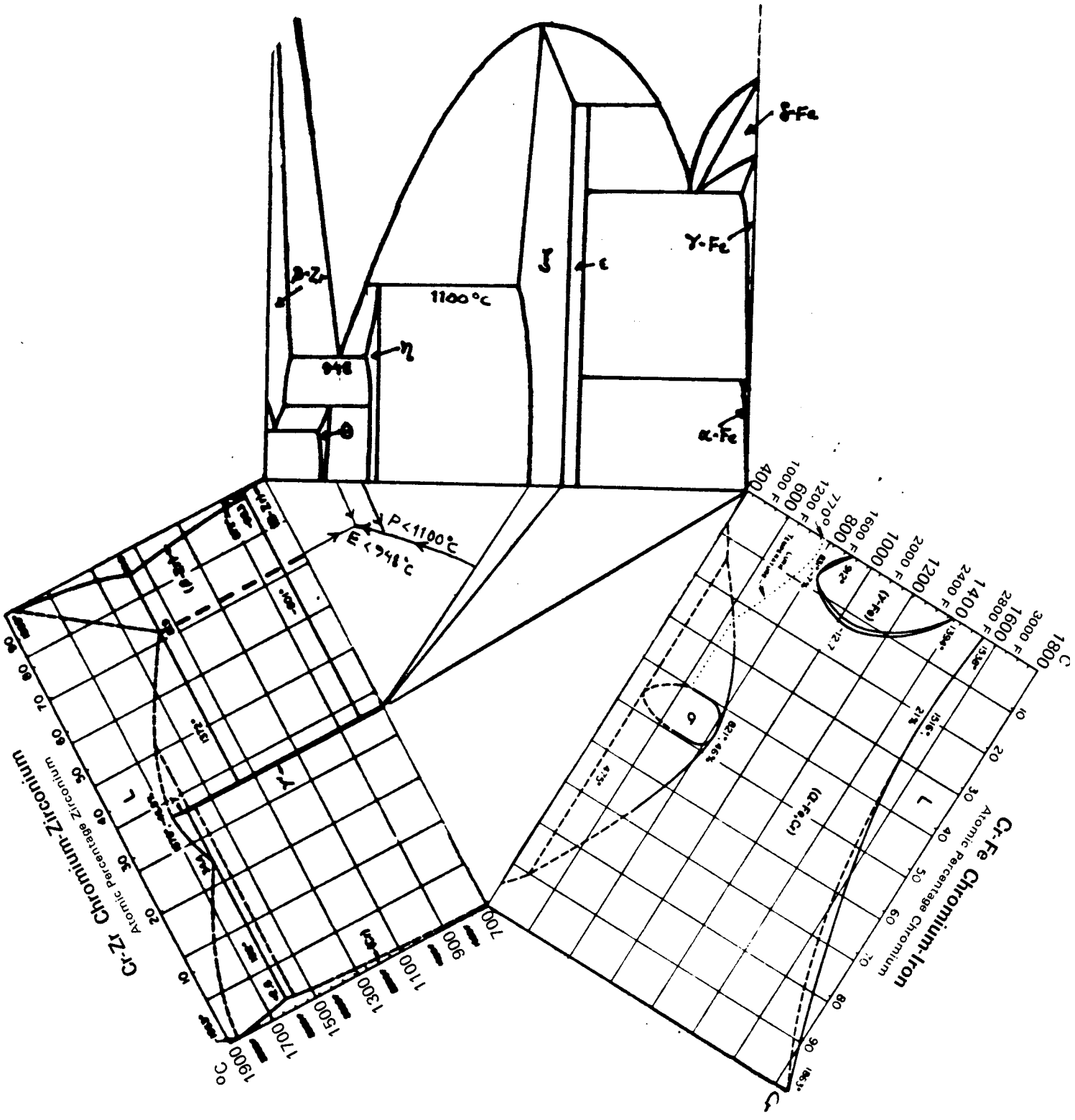


Fig 7. Ternary phase diagram Zr-Fe-Cr

diagrams (12, 13) for Zr-Fe and Zr-Cr, and the ternary Zr-Fe-Cr diagram (Fig. 7), that the $(FeCr)_2Zr$ phase is only surrounded by other solid phases at 1050 °C, which explains the limited reaction rate at that temperature. HIP experiments performed at 1100 °C with a pure Fe-canister resulted in a reaction zone about 3-4 mm thick.

This behaviour can also be explained from the binary diagram as the intermediate $FeZr_2$ phase melts peritectically at 1100 °C The experiments clearly show that Zircaloy can be HIPed together with stainless steel at a temperature of 1050 °C and that the interaction between these components is limited.

6.2 Interaction between Zircaloy and Inconel

Inconel is a nickel-chromium-based alloy used as spacer material. When Zircaloy hulls are HIPed together with Inconel at a temperature of 1050 °C for 3 hours, a 3-5 mm wide reaction zone is formed. The used piece from a spacer grid, which is made of a thin Inconel sheet, has completely reacted with the Zircaloy. The microstructure indicates that a large amount of molten metal was present at 1050 °C. This is also in agreememt with the binary Zr-Ni phase diagram (12) and the ternary Zr-Ni-Cr phase diagram (Fig 8).The reaction zone consists mainly of Cr_2Zr, $NiZr_2$ and Zr (Fig. 9). The Cr_2Zr is a primary phase formed on reaction with Inconel. The $NiZr_2$ phase is formed partly from the reaction with the Inconel, but also secondarily together with β-Zr from the molten metal on cooling. The Zr-Ni phase diagram (12) has three deep eutectica, which explains the extensive reaction of the Inconel at 1050 °C.

Inconel can be HIPed with Zircaloy at 1050 °C. A higher temperature increases the amount of melting in the system. An excessive amount of melting could penetrate the container wall.

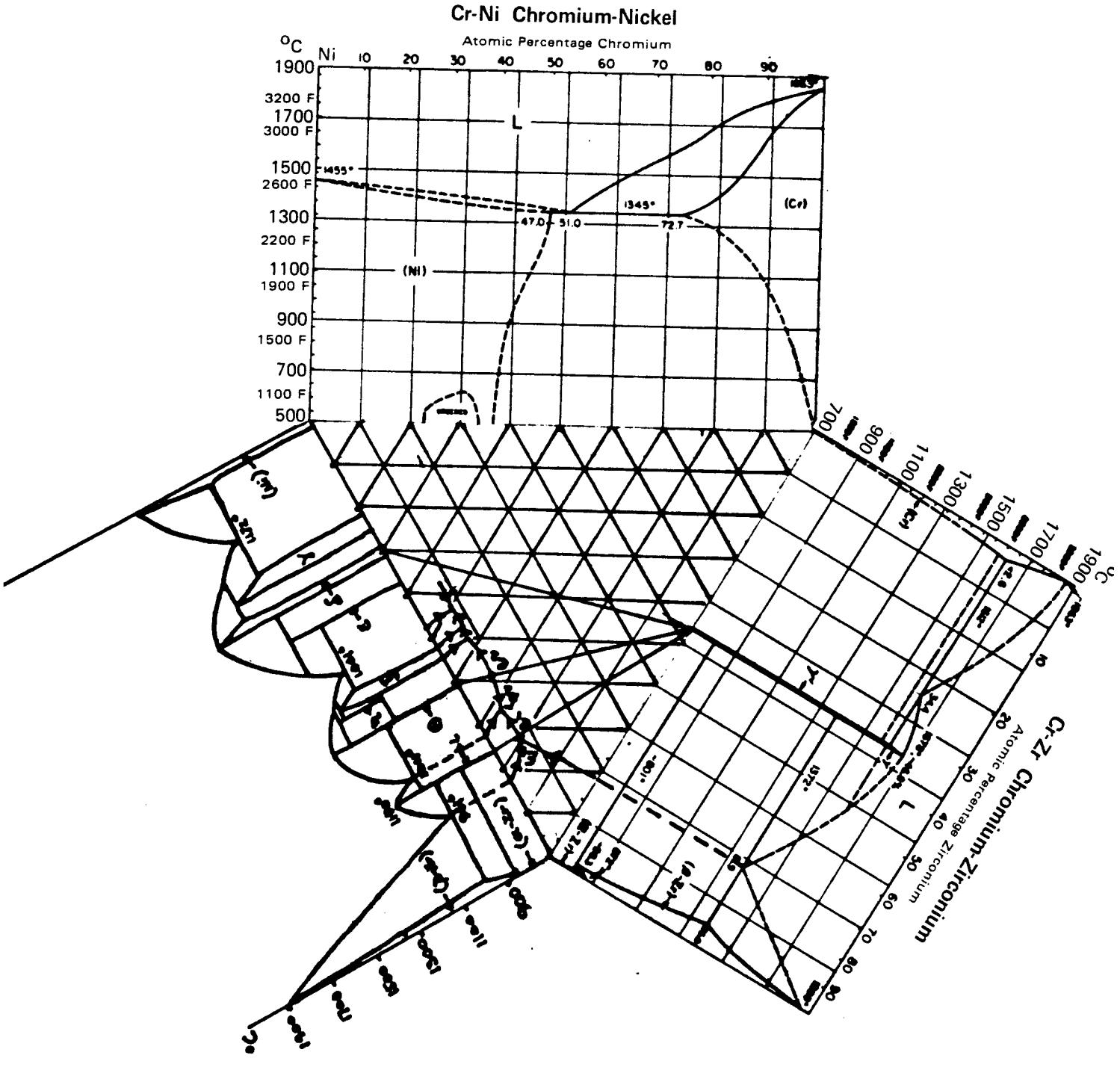


Fig 8. Ternary phase diagram Zr-Ni-Cr

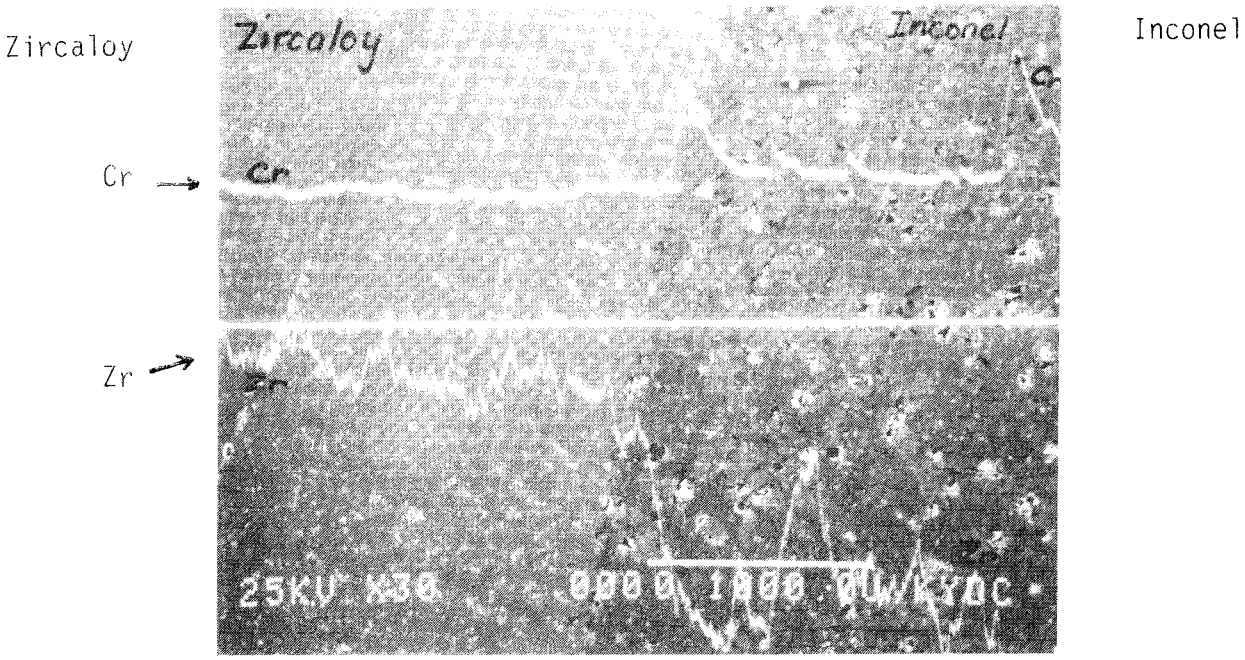


Fig. 9 a). Line analysis of Cr and Zr in interaction zone between Zircaloy (left) and Inconel (right).

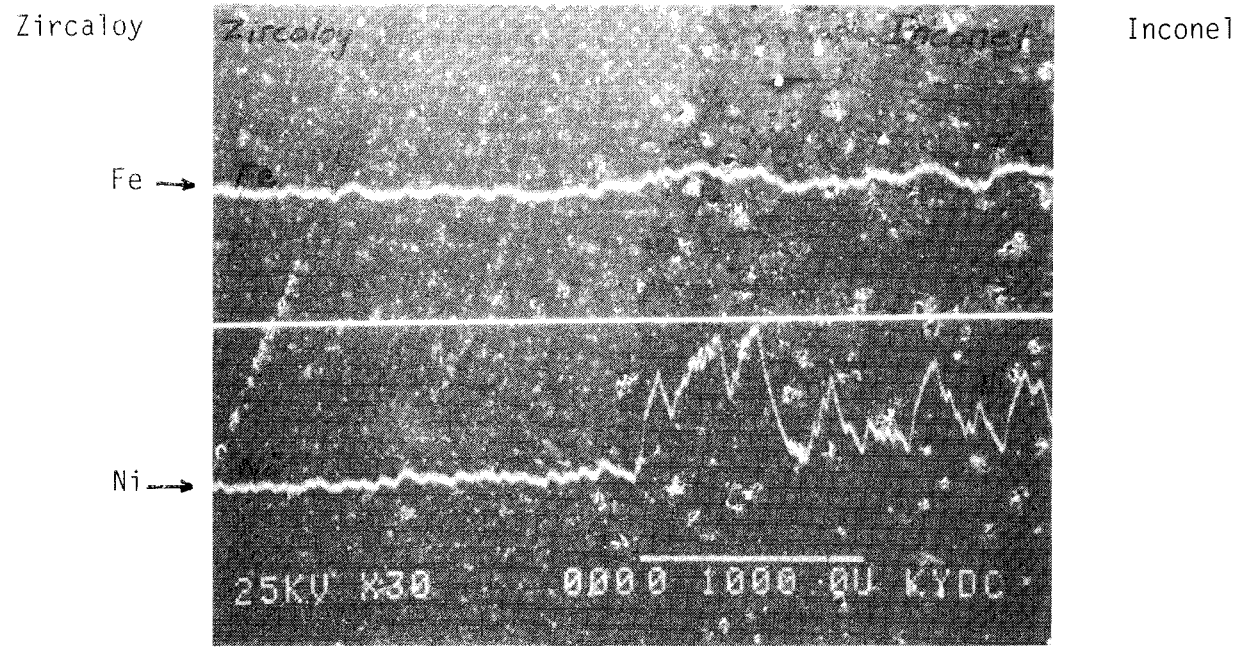


Fig. 9 b). Line analysis of Fe and Ni in interaction zone between Zircaloy (left) and Inconel (right).

7. BEHAVIOUR OF TRITIUM IN ZIRCALOY

Zircaloy hulls can be compacted to dense metallic bodies by HIP at elevated temperature. Since relatively large amounts of tritium in terms of radioactivity are present in the Zircaloy hulls (14), the releasing behaviour of tritium during HIP must be investigated. The goal is to keep the tritium release as low as possible. The waste system, mainly containing Zirconium (Zr) with some dissolved hydrogen (~ 100 ppm) and tritium (0.03-0.10 ppm), is heated during HIP to about 1300 K in a closed metallic container and subjected to an external argon gas pressure of about 150 MPa. Upon heating, a small part of the hydrogen, as well as the tritium, will escape from the hulls, diffuse through the container wall and contaminate the argon gas. Assuming that equilibrium prevails during the HIP process, the amount of tritium in the argon gas can be calculated. Further, the time required to approach equilibrium between the tritium in the hulls and the gas phase can be estimated by diffusion calculation. An equilibrium calculation the Zr-H-T-system is presented in APPENDIX I. Based on the expression in APPENDIX I for the relative amount of tritium released to the gas phase (eq 6), the following measures are recommended in order to minimize the tritium release to the compressed gas. The volume of gas in the HIP vessel should be as small as possible. The amount of hydrogen in the system should be kept low, since HT is the most stable tritium containing species in the gas phase. Finally, the HIPed Zircaloy waste should be allowed to cool to a relatively low temperature together with the compressed gas before the HIP unit is depressurized. Upon cooling, most of the tritium in the gas will diffuse back into the Zircaloy and the equilibrium pressure at the temperature when this process ceases will probably be several orders of magnitude lower. This means that 99.99 % or more of the tritium can be confined in the Zircaloy block after the HIP process. Fig 10 gives the calculated ratio T_{gas}/T_{tot} at different temperatures. The small amount of oxygen in the system will react with the Zr and form a solid solution of oxygen at the metal surface and thus prevent formation of water and tritiated water.

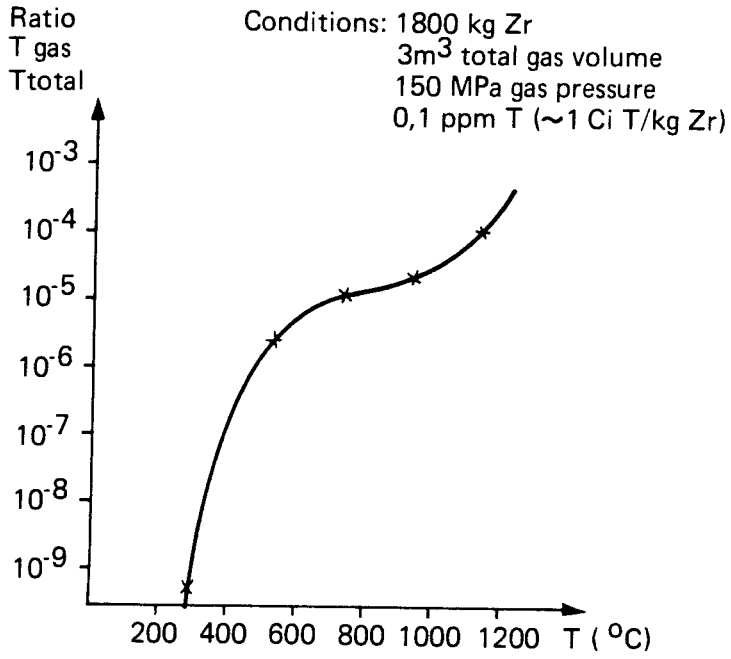


Fig. 10. Distribution of tritium in the compressed gas in relation to the total amount of tritium in the hulls in a HIP unit under the given conditions.

8. HIP OF ZIRCALOY HULLS IN BELLOWS-SHAPED CONTAINERS

A common characteristic of most particulate nuclear waste forms is that the relative fill density of the materials when packed in the container after only vibration or tapping is very low. Typical values for calcined products may be about 25 % of the theoretical density. Fuel hulls pack to a density of only 13-15 %. If material with such low fill density is packed in a sheet-metal cylinder of the usual type and then HIPed, a severe warping and an uncontrollable deformation of the container will result. There is also a high probability of container leakage due to the heavy deformation. A fill density of at least 50 % is usually required to avoid this problem.

The problem can, however, be solved by the use of an axially resilient sheet-metal container of the bellows-type, see Fig. 11. Upon application of an outside pressure to the sealed container, it will first compress axially. When the particulate material inside the container is compacted so that it offers a firm support to the sheet metal container, subsequent compaction of the container with its contents will be fully isostatic.

Depending on wall thickness and number of folds, the wavelength of the bellows-canister must be adapted to allow full axial compaction of the material inside. To obtain uniform compaction of the bellows, it is necessary to prevent material from intruding between the bellow folds on the inside. A screen of stainless steel is therefore placed inside the bellows. see Fig. 11. After being filled with hulls, the canister is welded and evacuated.

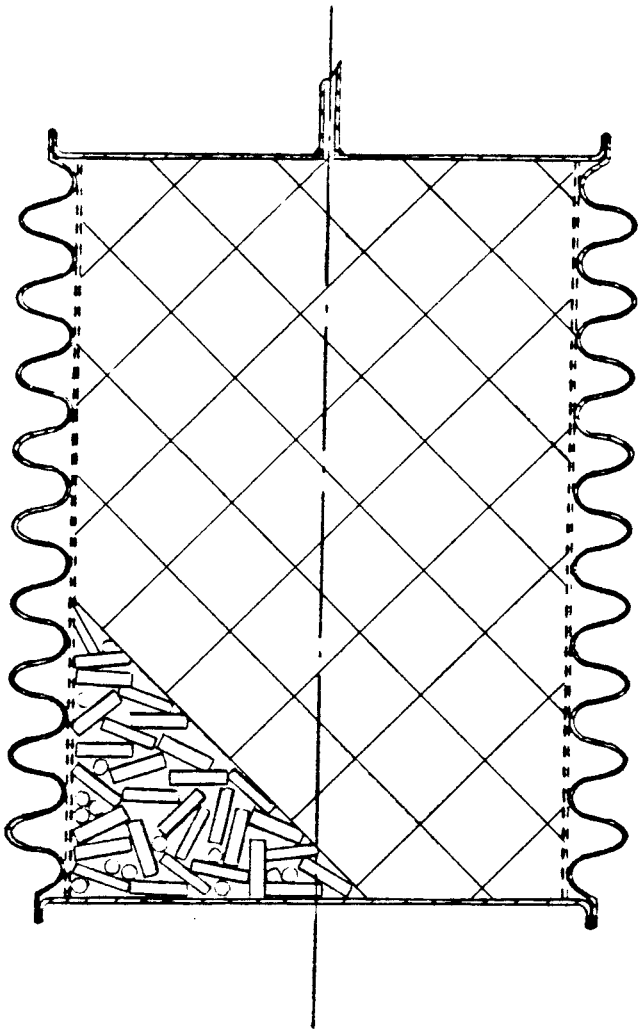


Fig. 11. Container of bellows type with a screen inside the bellows and filled with hulls.

In the tests performed two different types of bellows containers have been used. Both containers were of stainless steel of a type used for pipeline systems. Dimensions of the two containers before and after HIP are given in Table II. One was filled with 5.6 kg of Zr hulls and the other with 15.2 kg of Zr hulls. The hulls used in this study were made from tubes of Zircaloy II of a type used for BWR fuel elements in the form of thin-walled tubes with a diameter of 11.7 mm and a wall thickness of 0.8 mm. The tubes were black oxidized and treated as for fuel preparation. The tubes were cut into 25 mm long pieces by a cutting wheel and then degreased and washed in water.

A screen of stainless steel (dia 0.7 x 2.4 mm) was placed inside the containers to prevent hulls from intruding the bellows. After a complete axial compaction,the container wall occupies slightly more space than the material inside the container. The containers were therefore stretched to an appropriate length.

This type of bellow container is manufactured for use in pipeline systems as an axial expansion absorber. The containers are made with a single or multiple wall by means of a hydraulic expansion method. The multi-wall containers consist of individually welded tubes.

The bottom closure was welded on the container. After filling with the hulls and a slight vibration, the top lid was welded to the container. The two end lids were pressure-turned to ensure good weld and the top lid was also provided with an evacuation pipe. The canister air and absorbed moisture was then evacuated.

The container A was compacted directly by HIP and the gas was pumped cold into the press to about 60 MPa before the heat was turned on. Process parameters were 150 MPa and 1050 ^{o}C with a holding time of 3 hours. Density after HIP was measured at 6.55 g/cm^{3}, which is full density for Zircaloy. Fig. 10 shows the compacted canister cut in two halves. A reaction zone at the boundary between the Zircaloy and the stainless steel canister of one millimetre is visible.

Container B was filled with 15.2 kilos of hulls. The empty container is shown in Fig. 13. The container is 520 mm long. End lids were welded and made of 2 mm stainless sheet.

After filling with hulls, the canister was evacuated to 0.1 mbar. It was then cold isostatically compacted in steps of increasing pressure to study the cold deformation, see diagram in Fig. 14. After cold compaction to 50 MPa, the canister was hot isostatically compacted at 1000 ^{o}C and 150 MPa for 3 hours. Fig. 15 shows the canister after HIP. Density was measured at 6.55 g/cm^{3}, which is the same as for container A. The reaction zone of 0.5 mm between the Zircaloy and the stainless steel is slightly smaller than in container B.

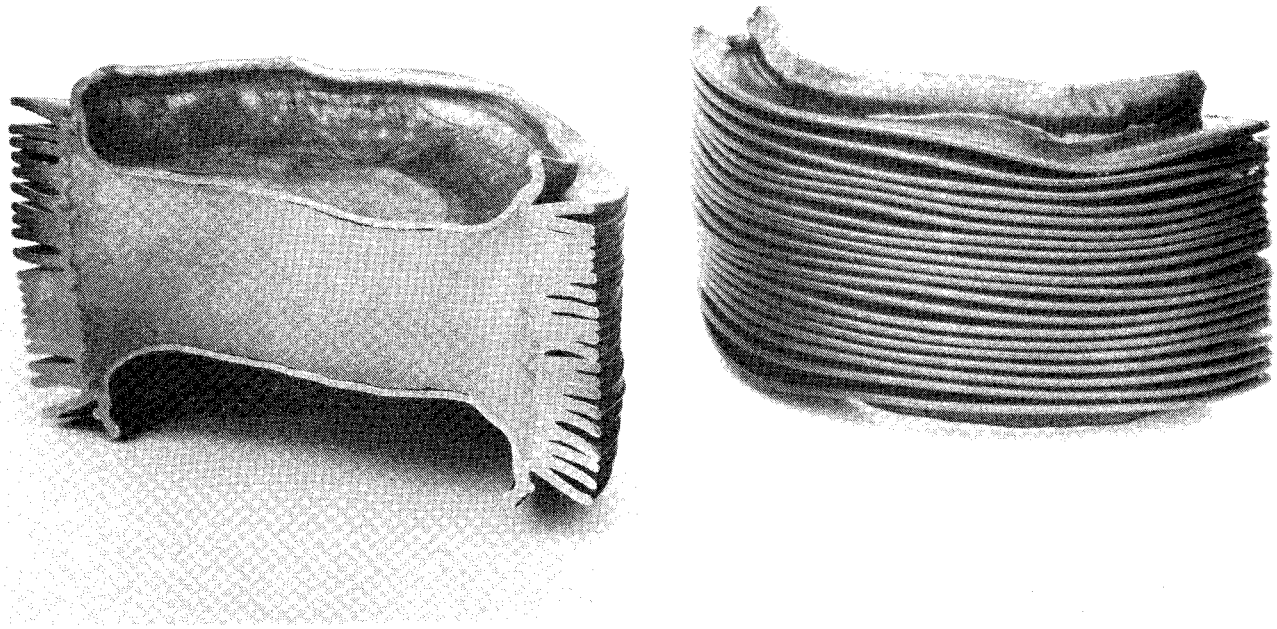


Fig. 12. Container A. The resilient bellows container was fully densified by HIP at 1050 °C for 3 hours at 150 MPa and cut to show the compacted hulls (5.6 kg).

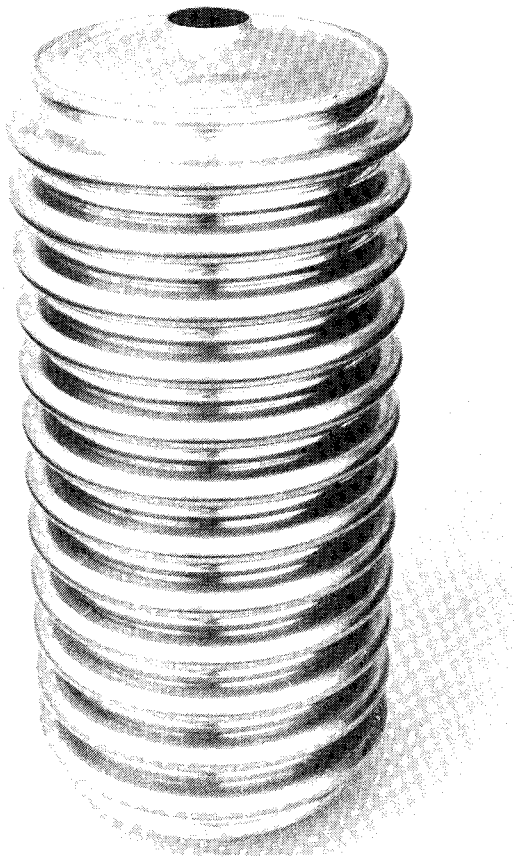


Fig. 13. Bellows-shaped container of stainless steel for HIP of hulls. The opening in the top is for filling with hulls.

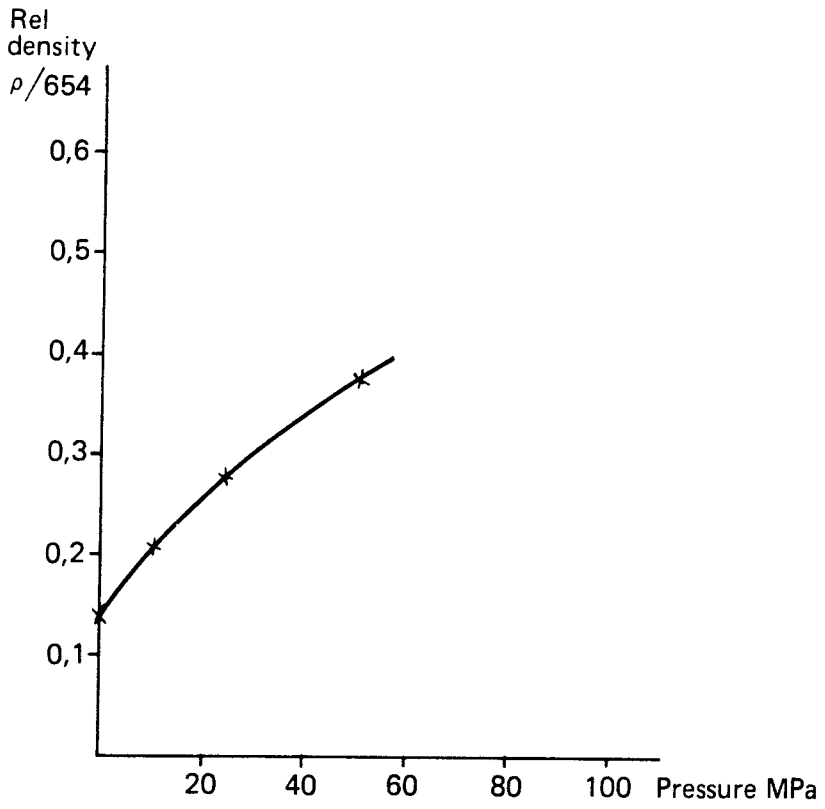


Fig. 14. Relative density of a bellows container filled with hulls and cold isostatically compacted as a function of pressure.

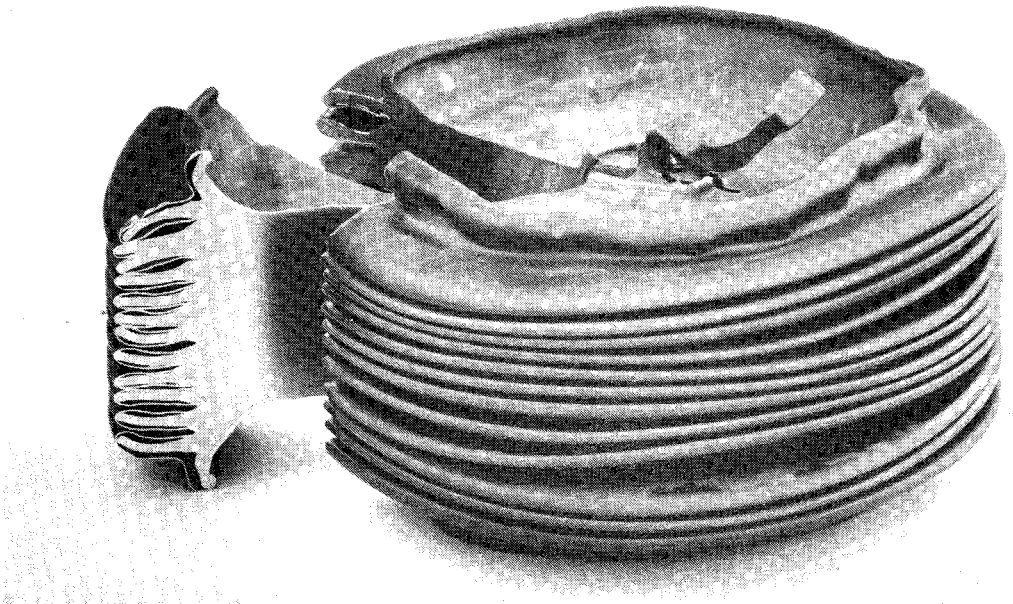


Fig. 15. Container B. HIPed at 1000 ^{o}C for 3 hours at 150 MPa. After HIP a wedge-shaped section was removed. The thin reaction zone between stainless steel and Zircaloy is visible.

CONCLUSION

The proposed bellows canisters can be used for HIP of uncompacted hulls. The screen prevents hulls from intruding between the folds of the bellows and a sound, uniform compaction is achieved. Both canisters tested reached full density. Examination of the HIPed hulls shows that the densification is complete and a very strong body of Zircaloy with a canister of stainless steel was obtained. The pressed containers showed no tendency to buckle. Nearly all of the compaction was axial. See table II. The reaction zone between the Zircaloy and the stainless steel of up to one millimetre does not seem to cause any problems. This is less than when Zircaloy reacts with a carbon steel canister.

Table II.

Data on bellow container before and after HIP at 150 MPa, 3 hours

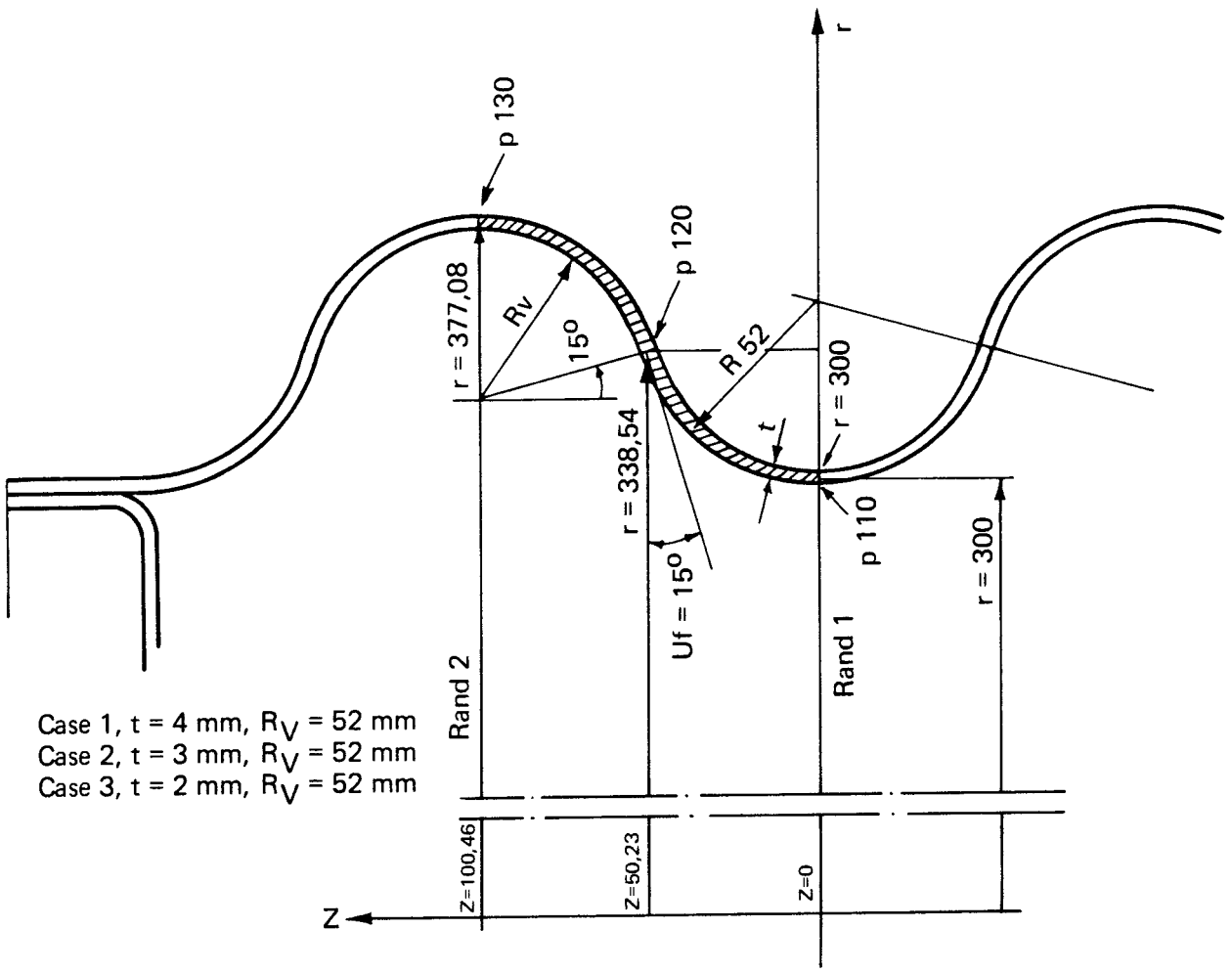
Dimensions (in mm)	Container A		Container B	
	Before HIP	After HIP	Before HIP	After HIP
Inside diameter	148	145	195	190
Outside diameter	185	185	260	260
Number of bellows folds	20	20	12	12
Thickness of lid	2	2	2	2
Thickness of wall	1.4	1.4	2.8	2.8
Inside length	340	46	513	78
Relative density	12 %	100 %	14 %	100 %
Weight of Zr hulls (kg)	5.6		15.2	
HIP Temp (^{o}C)	1050		1000	

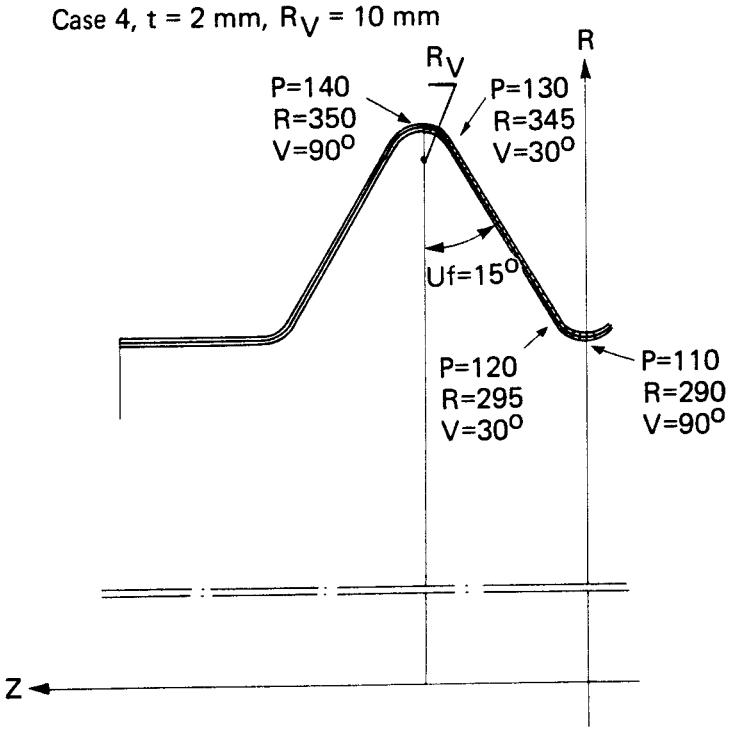
9. RISK OF BUCKLING OF BELLOWS CANISTERS

Bellows canisters of different geometric shapes have been analysed with respect to flexibility and margin against buckling. The model used was applied on a long closed tube with an outside diameter of 700 mm. The geometry of the corrugations and the wall thickness were varied according to Fig. 16 and the following material properties for titanium were assumed:

modulus of elasticity	108 GPa
yield stress	500 MPa

Flexibility was computed using an in-house computer program, designed for analysis of axisymmetric shells (internal ASEA designation: TO1042-TEXAS). The margin against ring buckling was estimated using a simple formula for an equivalent thin-walled tube subjected to external pressure, and the margin against local buckling in a fold was assessed by considering an "equivalent" tube subjected to a transverse bending moment (Ref. 15). The results shown in table III indicate that large flexibility is obtained when the corrugation amplitude is assumed to be large in relation to the corrugation wavelength. The modulus of elasticity is proportional to the safety margin against buckling. Stainless steel has twice as high a modulus of elasticity as titanium and consequently stainless steel has twice as large a margin against buckling as titanium. The estimated margin against buckling is sufficient in all cases considered.





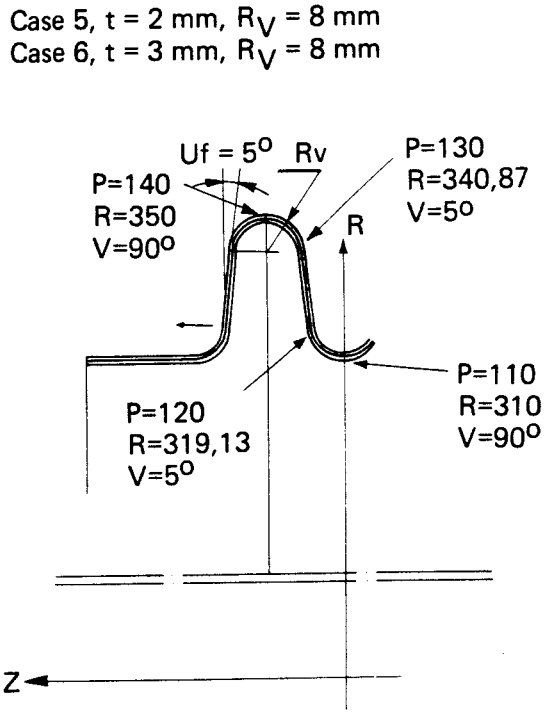


Fig. 16. Calculated shapes of corrugations.

Table III. Results of calculations of buckling safety margins for bellowsshaped HIP containers.

Case No	Wall thickness mm	Wavelength/2 mm	Amplitude mm	Calculation with pressure load 1 MPa			Scaled to max effective stress = 500 MPa		Buckling safety at σ_{emax} = 500 MPa	
				Edge load N/rad	Max effective stress MPa	Axial shortening mm	Pressure MPa	Axial shortening %	Ring buckling	Local buckling
1	4	100.5	77.1	71102	540	3.74	0.9259	3.45	> 10	> 10
2	3	100.5	77.1	71102	806	5.64	0.6204	3.48	> 10	9.9
3	4	100	200	61300	2553	69.1	0.1959	13.53	> 10	> 10
4	2	46.2	60	61300	3222	16.3	0.1552	5.48	> 10	> 10
5	2	16	40	61300	4594	18.6	0.1088	12.65	> 10	> 10
6	3	16	40	61300	2058	5.56	0.2430	8.44	> 10	> 10

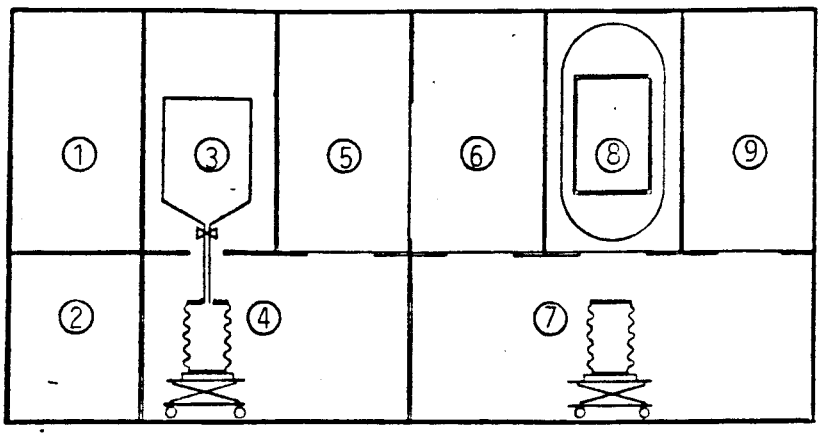
10. PRODUCTION PROCESS OUTLINE

The hulls ready for encapsulation are normally stored in water. Baskets with hulls are collected from storage and transferred to a position above the canister. The hulls and other small objects fall by gravity through a pipe into a canister also filled with water. After filling, the water in the container is sucked out through a drain pipe in the lower part of the container. A lid with evacuation pipe is then welded to the top of the container. Alternatively, if the hulls are stored dry in inert gas, canister filling can also be performed dry.

After the canister is filled with hulls, the top lid with evacuation pipe is gastight-welded. The canister is then evacuated during slow heating to dry the hulls. The canister is then evacuated and sealed. During evacuation, the gas must be filtered and cooled to remove dust and water vapour. The water in the bath is circulated continuously through the station's waste treatment system. The filled and evacuated canister ready for HIP goes to a transfer wagon. Check for contamination and, if necessary, decontamination must be performed before the canister with wagon can be transported to the HIP unit. The wagon has to pass through a gate from the hot cell with inert atmosphere out into the air. The canister is taken by the wagon to the position from which it can be loaded into the HIP press from below. The press is of the bottom loaded type. After being placed in the press, the canister is heated and the pressure is increased according to a predetermined schedule. Argon gas is used as the pressure transfer medium. The HIP pressure is set at 150 MPa and the temperature is set at 1000 ^{o}C. The dwell time at full temperature is 2-4 hours depending on canister size. The handling process is depicted schematically in Fig. 17.

A full size canister is thought to contain a volume of about 1-2 m^3. When the temperature and pressure of the HIP unit have been reduced, the container should be cooled down to almost room temperature in the HIP unit to allow the small amount of tritium released in the argon gas at high temperature to diffuse back into the Zircaloy during cooling. The cooled container is transported out of the HIP cell to intermediate storage.

The only equipment in this process which is not expected to be common practice in a reprocessing plant is the hot isostatic press. This unit, the HIP unit, which can be of ASEA QUINTUS press design, is of a type now used in production of high speed tool steel and superalloys. It is bottom-loaded and fully remotely operated, as in the production applications mentioned.



1. Intake of Zircaloy waste.
2. Intake of canisters.
3. Filling of canister with hulls.
4. Transfer wagon.
5. Welding and evacuation of canister.
6. Contamination check.
7. Transfer wagon.
8. Press for hot isostatic pressing.
9. Inspection and dispatch.

Fig. 17. Schematic illustration of waste and canister handling during encapsulation process.

11. CONCLUDING REMARKS

The conditions for densifying Zircaloy hulls from spent LWR fuel to solid blocks by hot isostatic pressing have been studied. It was found that HIP is an efficient method for compacting Zircaloy waste to fully dense and mechanically strong blocks with a minimum of handling. Fully dense bodies of Zircaloy were obtained at HIP temperatures of around 1000 ^{o}C at a pressure of 150 MPa for 3 hours. The HIP method requires only a few process steps, does not release dust or fumes and produces a product that meets all requirements for disposal of nuclear wastes.

One ton of leached hulls occupies an unconsolidated volume of 1.1 m^3 and has a free surface of 406 m^2 but has a HIPed consolidated volume of only 0.153 m^3 and a surface area of only 1.6 m^2, as calculated for a cylindrical container with a height of 1.5 times the diameter. The HIP process for hulls thus gives a volume reduction factor of 7, a surface reduction factor of 250 and a waste loading factor of close to 100 %.

Zirconium is highly resistant to corrosion in many different chemical environments (16). Corrosion rates of Zircaloy in quiescent distilled water have been measured to be 1 nm/year or $2 \cdot 10^{-9}$ g cm^{-2} d^{-1} and in sea water 10 nm/year (17, 18). Studies from Battelle show that most of the alpha activity is located on the inside surface of the hull and can be released by corrosion (7). This means that the zircaloy adds no protection against leaching of the radioactivity when, e g the hulls are incorporated into concrete. But by the compaction of hulls to large dense bodies,it is possible to exploit the excellent corrosion resistance of Zircaloy and obtain an efficient self-containment of the wastes in the hulls as well as a large reduction of corrosion-exposed surfaces.

Thermodynamic calculations have shown that the large amount of tritium present in Zircaloy hulls can quantitatively be contained in the Zircaloy phase. The calculations also indicate that the partial pressure of HT, which is the predominant tritium-containing species in the compressed gas, may be less than 10^{-11} atmosphere at a temperature of 600 K. The activity of the contaminated argon gas is therefore only $2 \cdot 10^{-11}$ Curie/cm^3 at normal pressure and temperature.

A study has been made of a possible process for industrial-scale application. Handling under water or in argon gas can prevent any fire hazard in the preparation sequence. The use of a special hermetically sealed double-walled metal container encase the hulls during densification in the hot isostatic press virtually eliminates the problem of permanent contamination of this equipment, thus greatly simplifying service and maintenance. One hot isostatic press can serve a reprocessing line with an LWR fuel capacity of 800 tons/year. Fines (residues) from fuel dissolution and alpha-contaminated ashes from incinerated organic materials in the plant may also be incorporated in the Zircaloy blocks.

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APPENDIX I

An equilibrium calculation of the Zr-H-T-system

The real waste system, containing many elements, is very complicated and equilibrium calculations have to be performed by a computer. Equilibrium computations were performed for the six component system Zr, Ti, Fe, H, T, Ar using the computer program SOLGASMIX developed by Ericsson (19). The results of these equilibrium calculations for different tritium contents and temperatures between 600-1400 K are published in detail in ref 20.

The amount of tritium released from the hulls to the gas phase can be calculated from a relatively simple expression by making the following approximations in the equilibrium calculation:

- the hydrogen and tritium enter the zirconium phase almost to a 100 % as a solid solution
- the only tritium-containing species of importance in the gas phase is HT
- the total pressure in the system is completely dependent on the amount of argon

The most important parameters influencing tritium release during HIP are the amount of tritium n(T), the amount of hydrogen n(H), the amount of zirconium n(Zr), the temperature T and the free gas volume V in the HIP vessel.

We must consider the equilibria:

$$H_2\,(g) \rightleftharpoons \tfrac{1}{2}H + H\,(Zr)ss$$

$$HT(g) \rightleftharpoons \tfrac{1}{2}H + T\,(Zr)ss$$

with the corresponding equilibrium expressions:

$$K_1 = a_H \cdot P_{H_2}^{\frac{1}{2}} \cdot P_{H_2}^{-1} \qquad (1)$$

$$K_2 = a_T \cdot P_{H_2}^{\frac{1}{2}} \cdot P_{HT}^{-1} \qquad (2)$$

The dilute solution of Hydrogen and Tritium in Zr behaves like a Henrial solution in the concentration ranges in question and therefore there is a constant temperature-dependent proportionality factor between chemical activity a and mole fraction x for small concentrations of Hydrogen and Tritium.

Therefore

$$a_H = x_H \cdot f_H \qquad (3\ a)$$

$$a_T = x_T \cdot f_T \qquad (3\ b)$$

where

$$RT\ \ln f_H = \Delta\bar{H}^E_H - T\Delta\bar{S}^E_H \qquad (4\ a)$$

$$RT\ \ln f_T = \Delta\bar{H}^E_T - T\Delta\bar{S}^E_T \qquad (4\ b)$$

The influence of temperature on the equilibrium constants K_1, K_2 is assumed to obey the relation

$$-RT\ \ln K_i = \Delta H_i - T\Delta S_i \qquad (5)$$

By using the ideal gas law and the definition of mole ratio, an expression for the relative amount of tritium released to the gas phase can be obtained.
With all the constants lumped together in the symbols A and ΔE, the expressions read:

$$\emptyset = A \cdot V \cdot T^{-1} \cdot n_H \cdot n_{Zr}^{-2} \exp(\Delta E/(RT)) \qquad (6)$$

With all parameters in SI units, the following expression is obtained:

$$\emptyset = 9.8173 \cdot 10^{-10} \cdot V \cdot T^{-1} \cdot n_H \cdot n_{Zr}^{-2} \exp(-119896/RT)$$

The expression gives accurate values for the relative amount of tritium release $\emptyset$ at temperatures up to 1135 K, where a phase modification from α to β occurs in the Zr phase. At temperatures below 600 K and at high H contents, the hydride ZrH forms (21) and thus the equilibrium

$$xHT(g) + Zr(H,T)ss \rightleftharpoons Zr(H,T)_x$$

will determine the TH(g) pressure in the system. The result of a calculation of Φ as a function of temperature is given in Fig. 10 in Chapter 7.

Diffusion of tritium in Zircaloy

In order to obtain chemical equilibrium in a system mainly consisting of H, T, Zr and Ar, where hydrogen and tritium are initially dissolved in the zirconium phase as a solid solution and the gas phase is pure argon, T and H have to diffuse through the zirconium phase out to the compartment containing the gas phase. First it must be pointed out that the amount of T and H in the gas phase at equilibrium is extremely low compared with the total amount in solid solution. The ratio oftritium or hydrogen in the gas phase to total tritium or hydrogen is between 10^{-4} and 10^{-9}, with the lower value at low temperatures (Fig. 10, chapter 7).

At equilibrium the predominating hydrogen species in the gas phase is H_2 and the predominating tritium containing species is HT.

If certain simplifying assumptions are made the time required to transport the trace amount of H and T from the Zr phase to the gas phase (e g the pressure medium argon) can be calculated and the reaction time that will give conditions close to chemical equilibrium in the gas phase can be estimated.

The first assumption made is that the flow of H and T is controlled by diffusion in the Zr (ss) phase and not by the rate of that reaction at the surface of the container. This assumption is believed to be true at temperatures above 500 K and is supported by many diffusion measurements performed on zirconium. The application of mathematical expressions derived from mass transport theory facilitates the interpretation of tritium flow in terms of fundamental material parameters. The mathematical expressions obtained are particularly convenient when the size of the specimens approximates semi-infinite media (22). The instantaneous mass release rate, L(t), from a semi-infinite medium is given at time t by

$$L(t) = A \cdot C_o \left(\frac{D}{\pi \cdot t} \right)^{\frac{1}{2}} \qquad (7)$$

and the cumulative mass release is given by

$$m(t) = 2AC_o \left(\frac{D \cdot t}{\pi} \right)^{\frac{1}{2}} \qquad (8)$$

where A represents the specimen surface area, C_o the initial bulk concentration of the diffusing species and D the diffusion constant.

It can be verified that the departure from a semi-infinite geometry diminishes when $Dt/R \rightarrow 0$ where R is the specimen radius. However the accuracy remains satisfactory for values of $Dt/R < 0.2$.

For eq 2 and 3a and 3 b it is assumed that the initial concentration C is uniform at $t = 0$ and that the surface concentration of the diffusing species is maintained equal to zero for $t > 0$.

At a temperature of 1000 K, the diffusivity of hydrogen in Zr is $3.3 \cdot 10^{-9}$ m^2 s^{-1}. With a specimen radius of 0.3 m, $Dt/R^2 < 0.2$ for times up to 1500 hours, which justifies the semi-infinite assumption. By comparing the cumulative mass release of T or H obtained from eq (8) with the amount of T or H present in the gas phase at equilibrium (eq 9), the time required to achieve chemical equilibrium with the gas phase can be estimated.

At a temperature of 1000 K the gas phase (argon) will at

equilibrium contain about $6.4 \cdot 10^{-6}$ kg hydrogen when the initial concentration of hydrogen within the zirconium phase is 0.91 kg m^3 (140 ppm). A large container with space for 2000 kg of Zircaloy hulls has a surface area of about 6 m^2. Rearrangement of eq (9) gives the release time

$$t = \frac{1}{D} \left(\frac{m \cdot \pi}{2AC_o}\right)^2 \qquad (9)$$

Incorporation of the above given values in eq (9) gives t less than one μs.

The calculation clearly shows that the time needed to fill the outer compartment with the equilibrium amount of hydrogen will be extremely short. In a real case the assumption that the surface concentration of H is maintained equal to zero at all times cannot be fullfilled and the real time needed to reach equilibrium will thus be several times longer than the time given by eq (9) as the amount of back-diffusion of hydrogen from the gas phase to the zirconium surface increases in importance when the hydrogen pressure approaches equilibrium values.

Comparing the temperature dependence of the diffusion of hydrogen with the temperature dependence of the Zr/H equilibria according to eq (6) shows that the time needed to achieve equilibrium conditions increases with temperature, as the amount of H or T in the gas phase increases faster than the diffusion rate for hydrogen in Zr. The diffusion calculations show that the very small amount of hydrogen and tritium present in the gas phase will very quickly reach equilibrium with the hulls, even at low temperatures.

The Zircaloy cladding from light water reactors contains about 0.1 ppm tritium with a resulting activity of ~1 Ci/kg Zircaloy. Above a temperature of about 400 ^{o}C, the tritium in the hulls can diffuse rapidly through the HIP container and enter into the surrounding argon gas and cause contamination problems. An inherent characteristic of HIP which is very valuable in this context, is that the gas volume surrounding the container is limited and closed. The wall of the pressure vessel, which is kept at a low temperature, cannot be penetrated by tritium. The maximum amount of tritium that can be found in the compressed gas (Ar) is determined by equilibrium conditions and is about 0.01 % of the total at the highest temperatures and much lower at lower temperatures.

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Uppsala September 1984

TR 84—10

Geochemical simulation of the evolution of granitic rocks and clay minerals submitted to a temperature increase in the vicinity of a repository for spent nuclear fuel

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TR 84-11

Smectite alteration

Proceedings of a Workshop Convened at The Shoreham Hotel, Washington, D.C., December 8—9, 1983
Compiled by Duwayne M Anderson
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TR 84-12

Formation of nitric and organic acids by the irradiation of ground water in a spent fuel repository

Hilbert Christensen
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TR 84-13

The corrosion of zircaloy 2 in anaerobic synthetic cement pore solution

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Glostrup, Denmark December 1984