

Recd from CT 4/20/00
CT said "This is a summary. Full paper is on its way."

Oxidation Phenomena in Severe Accidents (OPSA)

I. Shepherd^a, B. Adroguer^b, M. Buchmann^d, O. Gleisberg^d, T. Haste^a, P. Hofmann^c, Z. Hózer^f,
R. Hummel^a, R. Kaltofen^d, J. Knorr^d, N. Kourti^a, M. Leonardi^c, F. Oriolo^c, R. Schneider^d, L. Maróti^f,
L. Maus^f, G. Schanz^c, P. Windberg^f

- (a) Joint Research Centre, Ispra, Italy (JRC)
- (b) Commissariat à l'Énergie Atomique, Cadarache, France (CEA)
- (c) Forschungszentrum, Karlsruhe, Germany (FZK);
- (d) Technische Universität, Dresden, Germany (TUD)
- (e) Università degli Studi di Pisa, Italy (USP)
- (f) KFKI Atomic Energy Institute, Budapest, Hungary (AEKI)

SUMMARY

The objective of the Oxidation Phenomena in Severe Accidents (OPSA) project is to increase understanding of core degradation resulting from air ingress, the main concern being possible increased fission product release in reactor transients. Experiments in which oxidised fuel rods were exposed to air at high temperatures were successfully performed in the out-of-pile DRESSMAN single-rod and CODEX bundle facilities. These were supported by scaling studies which helped to define the test conditions with reference to possible plant conditions, and by detailed pre-test and post-test calculations with versions of the ICARE2 core degradation code modified for air ingress. The DRESSMAN tests showed a protective effect of oxide layers formed in steam before air ingress, with some increase indicated in the reaction heat after air ingress. The CODEX tests indicated acceleration of oxidation and core degradation phenomena following air ingress, with the extent of fuel rod/spacer grid degradation and of zirconium nitride formation depending on the transient conditions. Some UO_2 aerosol was observed in the second test in which much fuel melting and relocation occurred, but much less in the first in which the transient was stopped at the onset of rod failure. The project provides first, unique information on the impact of air ingress on core degradation, and indicates directions in which future work should proceed.

A. INTRODUCTION

The shared cost action "Oxidation Phenomena in Severe Accidents" (OPSA), FI4S-CT96-0031, started on 1 January 1997 and lasted 2½ years. It aimed to increase understanding of how air ingress into a reactor pressure vessel can affect the core degradation processes.

B. WORK PROGRAMME

Rationale

In their recent survey of air-ingress issues Powers et al. [1] considered that the most likely sequence of events leading to air ingress was during the late phases of a severe accident. Analysis of the Three Mile Island (TMI-2) accident shows that degradation is not uniform: the central regions of the core may melt and slump whilst the outer regions remain largely intact. Following rupture of the reactor vessel by molten debris, air may be drawn from the containment into the reactor vessel and react vigorously with these peripheral, largely intact rods. The impacts on reactor safety are:

- 1) vigorous oxidation of remaining cladding; oxidation by air yields about 85% more heat than steam (-755kJ/mole Zr c.f. -459kJ/mole Zr) and will further drive degradation;
- 2) UO_2 will be oxidized to U_3O_7 and U_3O_8 and the melting temperature of the fuel lowered;
- 3) volatilisation of fission products. Ruthenium is the main concern. Reactor accidents in a steam or hydrogen atmosphere release negligible ruthenium, but in a highly oxidizing atmosphere it can oxidize to volatile $RuO(g)$, $RuO_2(g)$, $RuO_3(g)$ and $RuO_4(g)$, as observed experimentally by Parker et al. [2] and by Iglesias et al. [3].

I-118

The toxicity of ruthenium worries those concerned with assessing nuclear plant safety. For this reason one of the future Phebus FP tests will be dedicated to the issue. The degradation aspects of air ingress had not, before the OPSA project, been assessed experimentally. All previous bundle tests (Phebus-SFD, CORA, PBF etc.) were performed in either steam, hydrogen or an inert atmosphere, none were performed in air. Without out-of-pile tests, such as here in OPSA, to calibrate the codes this Phebus test (FPTS) will be extremely arduous to prepare and it will be more difficult to persuade the relevant authorities of its safety.

Organisation of Project

The project was divided into five parts:

- 1) scaling studies - analysis of accidents in real plants in order to understand how air ingress accidents can occur with emphasis on making the experimental programme in this project as relevant as possible to reactor studies;
- 2) review of literature to examine phenomena and to identify reaction rates in air, where necessary these studies were complemented by separate effect experiments;
- 3) experimental studies, in particular two test programmes were completed:
 - a) 11 series of single rod tests in the DRESSMAN facility in Dresden, Germany,
 - b) 2 nine-rod bundle experiments in the CODEX facility at AEKI Budapest, Hungary;
- 4) pre-test calculations of both DRESSMAN and CODEX to support the experimental teams' efforts to produce feasible representative tests;
- 5) post-test analysis of the tests to determine how well the codes reproduce the experiments and to indicate areas of weakness that require further investigation.

C. MAIN ACHIEVEMENTS

C.1. Scaling Studies

The work to determine how an air-ingress transient will proceed in a reactor accident was based on the report of Powers et al. [1], where two main classes of scenarios were identified whereby air could enter the vessel:

- 1) the final stages of a severe accident with hot material resting on the floor of the lower plenum causing global or local failure of the lower head, Figure 1;
- 2) a shutdown sequence with or without an open vessel head, Figure 2.

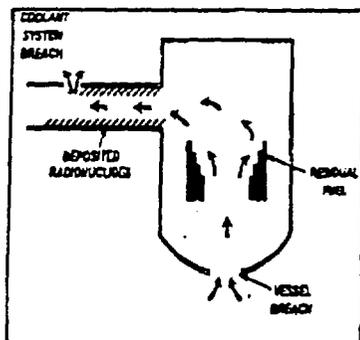


Figure 1: Melt-through Scenario

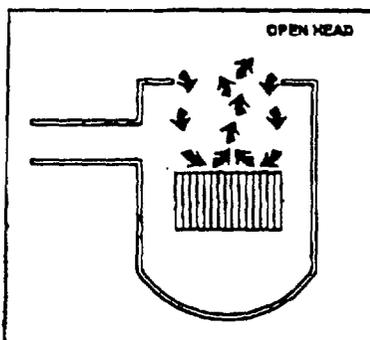


Figure 2: Early Phase of Shutdown Scenario

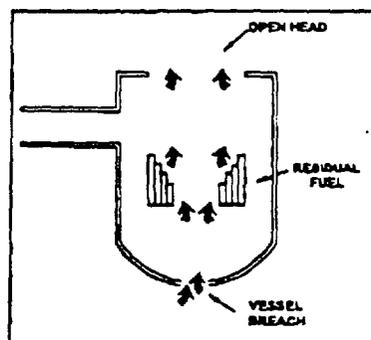


Figure 3: Late Phase of Shutdown Scenario

These are not mutually exclusive; combinations of the two could occur. Lower head failure may follow a shutdown accident, Figure 3, and the flow paths for natural circulation would then be significantly different. New calculations were performed considering these situations, in addition to those performed in the COBE project and reported there.

In midloop shutdown transients, steam from water boiloff in the core initially excludes air ingress, but later establishment of natural circulation could draw air into the upper core.

SCDAP/RELAP5 calculations for a transient based on the BETHSY 6.9c (ISP-38) test [4], but with no safety injection nor power shutoff, and with typical PWR fuel and control rods used, predicted that 70% of the metal would oxidise, but at a slow rate, and the fuel rods would keep their original geometry. Multidimensional analysis of in-vessel natural circulation using FLUENT5 for a further PWR mid-loop scenario gave preliminary information on the expected air concentration in the mixture flowing through different core regions.

In the vessel melt-through scenario, lower head failure could occur during the accident, connecting vessel and containment. Analysis based on a TMI-2 transient modified to give vessel failure shows that loop seal formation in the surge line prevents flow between the vessel and the open PORV. A calculation assuming surge line failure suggests that much more air is entrained from the containment atmosphere than with the surge line intact. Actuation of the High Pressure Injection System may lead to a new hydrogen excursion, followed by a cooldown phase; here the chimney effect is not predicted, because of surge line water sealing.

Potential air-fuel interactions inside the containment atmosphere after molten fuel ejection were calculated using FUMO-DCH [5], which considers competitive oxidation in air and steam. In a low pressure scenario, the interaction was mainly limited to the debris "flight time" until its deposition, which occurs only into the cavity. In high pressure scenarios, the debris is also spread outside the cavity, and air interaction is similar both in the cavity and in the rest of the containment. It is deduced that the cavity is not rich enough in air/oxygen, and even assuming its ingress into the vessel the related effects are expected to be significantly lower than the ones related to similar ex-vessel interactions with the ejected debris. The impact of core-concrete reactions was also considered in analysis performed outside the project of a French 3-loop PWR. Gas composition in the cavity was at first dominated by reaction of the corium with the concrete basemat. Air entered the pressure vessel when this had stopped and natural circulation between the containment and reactor cavity had started.

C.2. Calculational Support to CODEX and DRESSMAN Tests

The objectives of the calculational support were to understand the thermal behaviour of the facilities in different atmospheres, to advise on facility design, instrumentation and test conduct, and to analyse the experimental results. The main tool used for pre-test analysis was the CEA/IPSN core degradation modelling code ICARE2 V2mod2.2.

Code modifications

Initially the code was modified for air ingress phenomena, adding thermophysical properties of air, nitrogen and oxygen to the code's database, including kinetics for the Zircaloy/air [1] and Zircaloy/(Ar/O₂) [6] oxidation reactions, and accounting for the increased oxidation heat compared with that in steam. The modified code could model core degradation in air, steam and Ar/O₂ mixtures in different parts of the same transient, though not at the same time. It provided a satisfactory basis for the pre-test studies, using bounding analysis where necessary, and the flexibility in the modelling conferred considerable advantages.

DRESSMAN pre-test analysis

Scoping calculations performed to achieve a basic understanding of the facility showed that structural temperatures would remain within operating limits, and that small oxidation excursions might be possible in air alone (without pre-oxidation in steam). Such tests were excluded from the work programme. Commissioning tests were recommended, involving staircase ramps in air and steam, to help understand the heat balance. Analysis of these tests showed that the shroud was initially damp (from steam condensation), but dried out during the tests with hot argon. When this dryout was modelled (by modifying thermal properties of the insulator) good agreement with all the steady-state and transient data in both atmospheres was achieved. Evaporation of such water in the air tests could result in the oxidation taking place in an air/steam mixture rather than in air alone. The facility was modified by the DRESSMAN team with the aim of preventing water ingress into the shroud. First recommendations were made on the oxidation tests in steam.

CODEX pre-test analysis

The aim was to explore conditions for the air experiments and to suggest improvements in rig design and instrumentation. Firstly, the steam test CODEX-2 was analysed to improve understanding of the facility, using as a basis an input file supplied by AEKI. Good agreement with time of excursion and temperature histories was found when evaporation of water from the lower plenum was considered. Lessons learnt (timestep history, nodding, boundary conditions as appropriate etc.) were carried into the modelling of the AIT tests.

Initial AIT scoping studies gave a general understanding of the phenomena sequence and led to improvements to the facility. A very rapid excursion in air was predicted, faster than in steam because of the higher oxidation heat, faster kinetics and lower heat transfer to the fluid. The central unheated rod was originally envisaged as being empty but it was decided to pellet it to prevent its early excursion. The lower plenum needed protection from hot relocated material, melt detection was required at the bottom of test section, and thermocouples were needed in the upper and lower plena to define axial boundary conditions. Suitable changes to the facility were made by AEKI. Commissioning tests in argon were recommended.

Analysis of the commissioning data led to improvements to the model, and to good agreement with temperature histories of rods, shroud, insulator and offgas, showing that the calculated heat balance was reasonable. It was necessary to multiply the shroud thermal conductivity (porous ZrO_2) by a factor of ~ 2 (c.f. 1.75 for CODEX-2) to obtain the best radial temperature profile. This model was used for pre-test calculations for CODEX-AIT1 and AIT2, and for the limited post-test analysis of AIT1 described in section C.5.

C.3. Review of Phenomena and Oxidation Kinetics

Zircaloy oxidation in air has been reviewed. There are similarities with oxidation in steam due to the common reaction partner oxygen, but also considerable differences. The higher exothermal energy causes a more pronounced temperature escalation. After initial growth of protective oxide scales, localised loss of scale protectiveness ensues, leading to increased oxidation rates. Radial surface cracks form in the oxide layer and then in the α -Zr(O) layer. A nitrogen-rich phase (ZrN) forms in the oxide near the boundary with the α -Zr(O) layer, leading to the growth and spreading of breakaway oxidation and less protective sublayers. Thus, the presence of nitrogen has a strong influence on the degradation of the cladding. These observations, such as the change in kinetics (cubic to linear time dependence) and oxide microstructure, are being quantified by a series of small-scale thermogravimetric experiments in progress at FZ Karlsruhe, outside the OPSA project.

The current project does not cover detailed model development based on this new understanding. Instead, the traditional approach of parabolic kinetics as used for steam oxidation (where the oxide layer for a long time remains protective and therefore this time dependence has some physical foundation) has been employed. Powers et al. [1] noted a wide spread amongst existing air oxidation data, which were fitted to parabolic rate laws. One of these, designated "NUREG1", based on existing data above 1000°C, was used in plant calculations [7] carried out with a modified version of MELCOR [1], the results of which formed much of the basis for the OPSA project. A second, "NUREG2", with a higher activation energy, was consistent with measurements carried out at AEKI during the present project. A third correlation, here termed "NUREG-B", about eight times NUREG1, was used as an upper bound, approximately consistent with the peak data noted in [1].

C.4. The DRESSMAN Experimental Programme

Facility description

The DRESSMAN facility is built round a single Zircaloy-clad fuel rod simulator of heated length 0.42m, filled with annular ceramic pellets and powered by an internal tungsten bar heater. This is surrounded by a fluid channel, insulating layers of high-density alumina and layers of fibrous insulating material. The insulator is sheathed by a stainless steel shroud and cooling coils through which cold water is pumped at 20-21°C. The whole assembly is inside a steel

containment. Coolant injected into the lower plenum through an annular inlet nozzle surrounding the rod flows upwards over the cladding, radially out over the top of the insulators, down over the cooling coils and finally out through a vent at the bottom of the plenum. Steam condenses on the cooling coils and the resulting water follows the same path out of the facility. The computer-controlled electrical power supply operates manually, or by servo to give a preset temperature history at one point on the rod. Temperatures are measured by thermocouples on the clad at three axial locations, and in the insulator at three radial positions. A ratio pyrometer monitors the rod surface temperature.

The test programme

Four commissioning tests were performed, two in argon and two in steam, with staircase ramps to up to 1000°C, to help understand the thermal response and as a basis for the modelling work. These led to improvements to the facility and test procedure, e.g. shielding the shroud to help prevent water ingress, and dismantling and drying out the insulation before each test. Analysis demonstrated that heat losses from the single rod were high, but the power supply and temperature control systems were sufficient to achieve the desired test conditions.

The test sequence consisted of thermal stabilisation in steam at 500°C, heatup at 1K/s to 1500°C, oxidation in 0.8g/s steam for 100-600s, then either cooldown, or oxidation in 0.2g/s air followed by cooldown. Three tests were performed (to check for repeatability) with ZrO₂-pelleted Zircaloy-4 cladding for each of the conditions: pre-oxidation in steam only for 100, 200, 300 and 600s; pre-oxidation in steam for the same periods then 600s oxidation in air. With the hottest 80mm length of the pellet stack replaced by UO₂ pellets, 3 tests were performed with 100s steam oxidation and 600s air oxidation, and 2 with 200s preoxidation. Finally, a test was carried out with the UO₂ pellets but with part of the cladding removed. About 30 tests in all were performed.

Post-test examination and energy balance

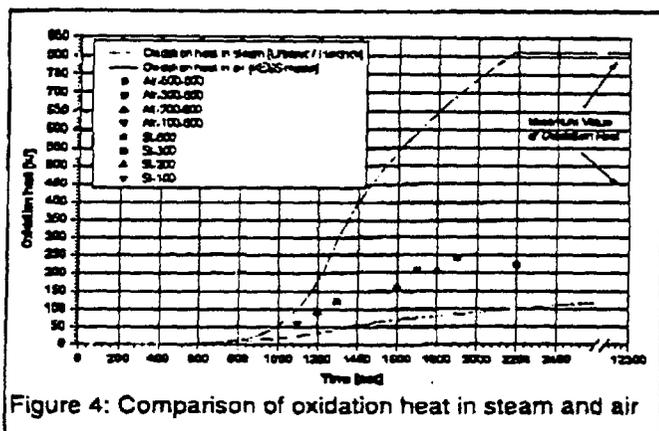


Figure 4: Comparison of oxidation heat in steam and air

Oxide layer thicknesses were measured (12 to 16 specimens per test) by a microscope after embedding the specimens in epoxy resin. Radial and axial cracking of the oxidised layers was observed, more for longer oxidation, and with loss of cladding fragments (spalling) in the air tests. Apart from this, the air oxidation led to no apparent difference in the appearance of the specimens. Since there was so much breakaway oxidation, the total oxidation of the specimens was determined by fitting

curves through the measured axial distributions of layer thicknesses, and integrating the results to give the total volume of oxide formed, and hence the heat of reaction. The oxidation heat was also estimated using a "black box" method, with MATLAB/SIMULINK. The measured oxidation heat was compared with that calculated by KESS for steam using the Urbanic-Heidrick correlation [8]. Figure 4. It was concluded that the heat production in air was up to 30% higher than in steam, but this was less than expected, similarly for the rate of increase in oxide growth when air was introduced. Thus, the influence of pre-oxidation in steam must be considered. Under the conditions of the DRESSMAN experiments, the main contribution to the total heat of reaction came from oxidation in steam rather than in air; the period in the steam atmosphere was such that most of the metal had been oxidised by the time air ingress occurred. The tests with UO₂-filled rods led to no significant additional conclusions. In the one where part of the clad was removed, oxidation by air of the tungsten heater, giving tungsten trioxide, led to the formation of low melting point W/Zr/U/O compounds and thereby some melting and relocation below 1700°C.

C.5. The CODEX Experimental Programme

Facility description

CODEX was built to investigate the behaviour of small fuel bundles in severe accident conditions. The AIT tests used 9-rod square PWR-type bundles with 2 spacer grids; the 8 peripheral rods were heated electrically with tungsten bars over 600mm length. The central unheated rod was used for instrumentation. The clad was Zircaloy and contained annular UO_2 pellets, the shroud part was made of 2mm thick Zr2%Nb alloy. Around the shroud ZrO_2 thermal insulation was added. The test section was connected to the preheater and to the cooler sections laterally at the lower and upper ends respectively. Another junction at the lower end enabled injection of cold, room temperature, air. For the investigation of aerosol release a cascade impactor system was connected to the upper plenum of the cooler, and two pipelines allowed continuous aerosol measurement by laser particle counters.

CODEX-AIT1

Initially, a commissioning test was performed on the AIT1 bundle in argon, with a succession of power ramps including a controlled spike at the end of each ramp designed to give a linear ramp+hold temperature history at the top of the unheated rods. The maximum temperature reached was 1020°C. The data were used for refinement of the ICARE2 model for pre-test calculations for the main AIT1 experiment.

The main CODEX-AIT1 test was designed to simulate the top of the outer region of the core remaining following a TMLB' from full power, surge line failure, melting and relocation of central core region, subsequent lower head breach and cold air ingress by the "chimney effect". Detailed calculations with the air version of ICARE2 V2mod2.2 led to the following test protocol being recommended:

- 50±10µm pre-oxidation at 900-950°C in hot 75%Ar/25%O₂ (650°C);
- then 3.5g/s air injection at -20°C;
- followed with heatup at ~0.5K/s by an electrical power ramp;
- termination of the subsequent transient at peak temperature of 2100°C or on evidence of melt detection, by shutdown of power and replacing air by cold Ar flow.

The use of argon/oxygen was to prevent hydrogen generation. The calculations indicated possible oxygen starvation above the flame front, reducing the chance of fuel volatilisation.

AIT-1 was performed according to the proposed scenario, but with the preoxidation starting at a slightly higher temperature than planned. The oxidation heat produced at this temperature could not be compensated by reducing the electrical power. As a result, a strong temperature excursion reaching -2200°C took place during this phase which could be stopped only by injecting cooling argon gas. After stabilization of the rods at about 900°C, air injection started and a second temperature excursion ensued. The test was terminated as planned by replacing the air by argon and turning off the electrical power at 2100°C, to prevent large-scale bundle degradation. The air ingress phase lasted about 500s. Aerosol particle counter data showed a peak in both excursions.

The final bundle state showed strong oxidation of rods and shroud (up to 550µm oxide thickness), strong nitriding (up to 300µm ZrN), limited rod failure, local melting of the clad, and failure of the upper spacer grid. At the bundle top limited pellet/clad interaction occurred in 5 rods, with interaction layers of 50-130µm. Rod-like geometry was mainly preserved. Analysis of impactor data showed only negligible release of UO_2 to the offgas (a few tenths of a µg), a consequence of the bundle damage being small; Zr and Sn (from the clad), and Nb (from the shroud liner). Some impurities from the shroud materials were also detected in the aerosols.

Limited post-test analysis was performed with the air version of ICARE2 V2mod2.2 to help in the preparation of AIT2. A prescription was found (Ar/O₂ kinetics*1.8, air kinetics consistent with NUREG1*0.8) which could reproduce the main features of the experiment (temperature histories of rods and shroud, offgas, initial observations of bundle state etc.) and therefore was suitable for the AIT2 test definition. The NUREG2 kinetics gave too little oxidation in air, while NUREG-B gave

too much. The event sequence of AIT1 was summarised as:

- localised excursion in Ar/O₂ (local hotspot or oxide breakaway on the centre rod?) with slight relocation of eutectic (<1% UO₂); evidence from temperature radial inhomogeneity, and cool offgas;
- calculated oxide thickness range at this stage 80-140µm at top of bundle;
- possibly then cracking of oxide caused by the rapid cooling in Ar, and limited dissolution of oxide in the Ar plateau;
- then excursion in cold air from as low as 900°C, without a power increase;
- the hotter offgas suggests more widespread oxidation than in the Ar/O₂ excursion, but no evidence of large-scale relocation; escalation at top grid.

The overall conditions attained were not favourable to significant fuel volatilisation since only a small amount of fuel was exposed to oxygen, but there was a need to be conservative in the first experiment.

CODEX-AIT2

To give a higher chance of U-bearing aerosol release, the AIT2 test was allowed to proceed to more severely degraded state. Use of steam rather than Ar/O₂ for pre-oxidation can avoid an excursion and is more prototypic of a reactor accident. The proposed test sequence was:

- a thermal stabilisation phase at 600°C;
- pre-oxidation in Ar/steam mixture in two stages at 820°C and 950°C to give 20-25µm oxide;
- cooling to 820°C and flushing with hot Ar;
- changing to cold air and ramping at 0.5K/s until the oxidation excursion starts;
- termination on evidence of melt reaching the lower parts of the bundle, by turning off the power and replacing the air supply by cold Ar.

As before, detailed ICARE2 calculations were performed to aid in the selection of the test protocol, and again the possibility of oxygen starvation above the flame front was predicted. Test conduct followed the proposed scenario, except that due to a valve leak a small air flow joined the steam/Ar mixture during preoxidation. Temperature excursion was observed on the fuel rods to a maximum indicated temperature of 1900°C, similarly on the shroud, Figure 5.

Air injection was stopped when the central elevation reached 1700°C, indicating melting. Aerosol samples were taken using impactors before the preoxidation, before the air ingress phase, during the temperature excursion in the air ingress period and in the cooldown phase. Video recording through an observation window below the elevation of the upper spacer grid showed melt relocation during the air phase. The particle counters were activated after the preoxidation phase. The peak in the aerosol release was at least 3 times more than in AIT1.

In AIT2 the bundle damage was more severe than in AIT1, high temperature conditions were kept for longer, the exposure to air being ~1000s. Much relocation of fuel took place from the top of the bundle, leading to blockage near the bottom, Figure 5. The maximum oxide thickness of 120-160µm was measured in the middle of the bundle. Nitride formation was less than in AIT1, only up to ~30µm, but was seen over more of the bundle. Pellet-clad interaction was seen on all rods in the hottest part of the bundle, above 280mm, with interaction layers of 50-170µm. The structure of the UO₂ pellets changed in some places, there were cracks between the fuel grains, and the fuel powderised, probably due to the oxidation. In both tests, pyrometer readings and the bundle final states were consistent with fuel degradation occurring in air at up to 2000-2100°C.

About two orders of magnitude more uranium were detected in the aerosol released in AIT2 than in AIT1. In the AIT2 samples uranium was found both in single particles (1-3µm) and in aggregates (10-15µm). The shape of the particles was mostly rectangular. The aggregates had elongated or irregular forms and contained other elements such as Si, Al, Fe beside U. The total uranium release from the bundle was estimated as 50-100µg, entirely as UO₂ with no higher oxides detected. The amount corresponds to theoretical calculations.

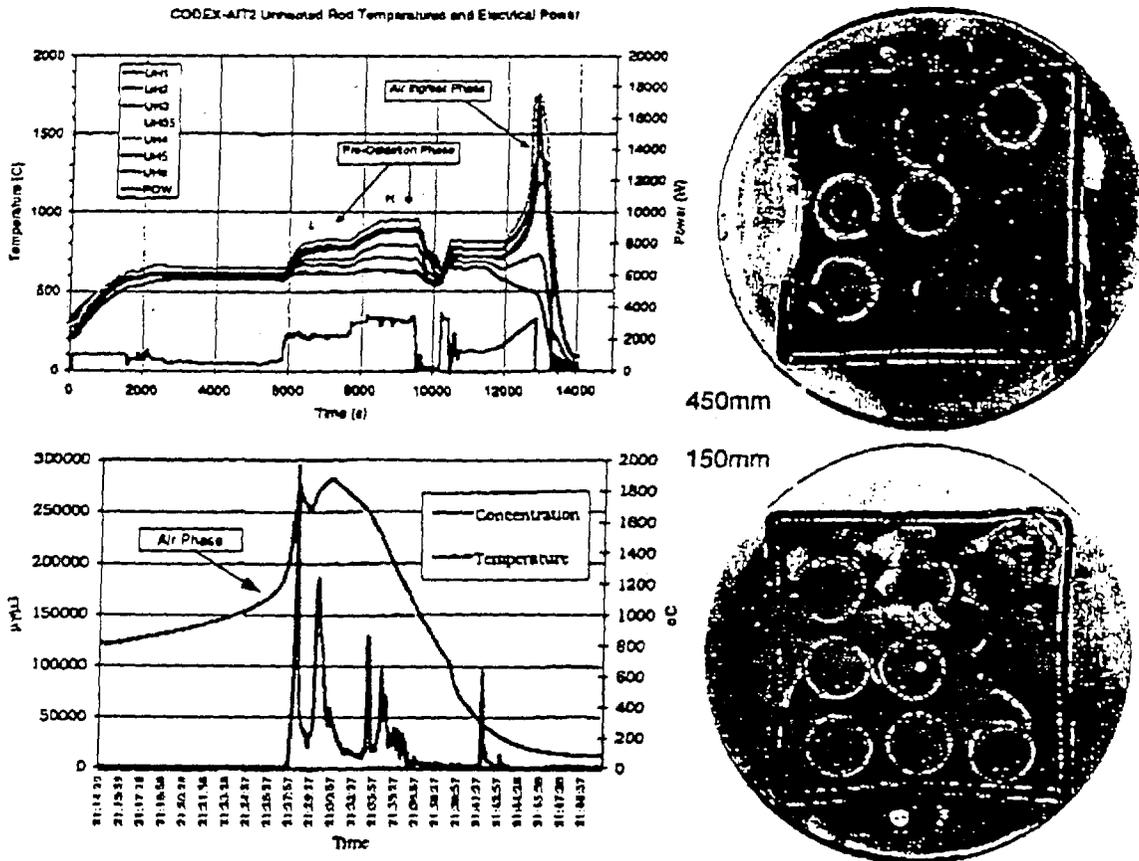


Figure 5: CODEX AIT2 Unheated Rod Temperature Histories, Aerosol Production in Air Phase and Cross-Sections showing Rod Degradation and Material Relocation

Summary

The CODEX air ingress tests indicated the acceleration of oxidation phenomena and core degradation processes during the late phase of the vessel melt through accident, when the air can have access to the residual fuel bundles in the reactor core. The degradation process was accompanied with zirconium nitride formation and release of U-rich aerosols. The two experiments with slightly different conditions gave rather different results regarding the extent of fuel rod and spacer grid degradation and relocation, the axial temperature profile, the amount of nitride formation and U-release and the conditions of the temperature excursions.

C.6. Post-Test Calculations

Post-test calculations were performed with the latest version of ICARE2, namely V3mod0.4, to evaluate its ability to reproduce the general behaviour of Zircaloy clad exposed to oxidation in air. The air models developed for V2mod2.2 were included, and the air oxidation model was extended to parallel multi-channels and debris bed configurations. Moreover, according to the new numerical scheme chosen in ICARE2 V3mod0.4, such an oxidation module has been implicitly coupled to the thermal hydraulic module.

ICARE2 V3mod0.4 was used to simulate CODEX-AIT1 and AIT2, as well as DRESSMAN tests with 300s oxidation in steam followed by 600s in air. Due to experimental uncertainties on some test boundary conditions (real composition of the carrier gas in AIT2, state of the shroud insulator in DRESSMAN), the conclusions below were drawn mainly from the AIT1 validation.

The oxidation kinetics used in the argon/oxygen environment (pre-oxidation phase) led to a slight under-estimation of the clad temperatures; a corrective factor of 1.6 gives a perfect fit to the bundle thermal behaviour. The NUREG-B and NUREG2 air oxidation kinetics were tested; they

