ABSTRACT

Boron carbide (B₄C) is widely used as an absorber material in many commercial reactors, such as boiling water reactors, Russian VVERs, later French pressurised water reactors, and planned to be used in the European Pressurised Water Reactor (EPR). Under hypothetical severe accident conditions, B₄C reacts with its surrounding stainless steel cladding, producing eutectic melts above 1200°C; remaining bare B₄C and B₄C/metal mixtures are then exposed to steam and oxidize highly exothermically. As well as hydrogen, gases and aerosols containing boron and carbon compounds are produced, which affect the transport and deposition of radiologically important fission products such as iodine and caesium in the circuit, and subsequent behaviour in the containment.

The influence of a B₄C control rod on fuel degradation and fission product release through to the late phase, material transport in the circuit and behaviour in the containment was studied in the nuclear-heated integral experiment Phebus FPT3 performed by IRSN at Cadarache. Carbonaceous gas production was monitored, and evidence for substantial deposition of B-containing compounds in the circuit was gathered. The electrically-heated QUENCH-07 and -09 tests performed by KIT at Karlsruhe used similar bundle geometry and similar but less severe test conditions, with a fast cooling phase. Extensive separate-effects tests on oxidation of B₄C and its interaction with surrounding materials have also been performed by IRSN (BECARRE programme) and KIT (BOX, LAVA, QUENCH-SR).

This paper compares the phenomena involving B₄C observed in these experiments, concentrating on degradation, transport and deposition behaviour. In particular, there is evidence concerning blockage formation in the hot leg of the FPT3 circuit, which affects the transport of fission products, and this is supported by similar observations in the separate-effect tests. Possible explanations for the phenomena observed are advanced, and suggestions for further work to improve understanding in this area are put forward.
1 INTRODUCTION

Light water reactors use boron in large quantities and in a variety of forms to act as a neutron absorber. Boiling water reactors and some pressurised water reactors use stainless-steel-clad boron carbide (B₄C) control rods. Under severe accident conditions these would rupture, and reaction of the B₄C with steam would produce gases and aerosols containing boron and carbon compounds, which affect the transport and deposition of radiologically important fission products such as iodine and caesium in the circuit [1], their subsequent behaviour in the containment, and hence the potential source term to the environment. This paper draws together recent integral and small-scale experiments involving B₄C exposed to steam under severe accident conditions, comparing and contrasting the results, with emphasis on circuit phenomena.

2 INTEGRAL EXPERIMENTS

2.1 Phelbus FPT3

The in-reactor integral Phelbus FP tests studied bundle degradation and release, transport and deposition of fission products, structural and control rod materials in the model primary circuit and containment building, under steam-rich or steam-poor atmospheres, and under low pressures (~0.2MPa), with specific attention to the behaviour of fission products. The final test FPT3 [2], [3], studied especially the impact of a B₄C control rod on fuel degradation, fission product transport/deposition in the circuit and behaviour in the containment, using fuel irradiated to 24.5GWD/tU, and featuring a steam-poor period. The experimental facility, scenario, and objectives of the series have been extensively presented in the literature, for example [4]. The FPT3 test sequence involved heating of the bundle through a succession of power ramps and plateaux, leading to an oxidation runaway, further ramps and plateaux leading to fuel melting and relocation, with the degradation phase being terminated by reactor shutdown about 5hr after the beginning of the heating phase.

Rupture of the control rod occurred during the first major power rise (guide tube temperature ~1450°C at 500mm elevation), followed shortly after by the first appearance of CO in the containment. Carbon dioxide arrives later, at the end of the first oxidation phase when the hydrogen concentration is decreasing in the main circuit line (see the H₂ production in Figure 1, which well illustrates the FPT3 degradation events). Carbon monoxide production dominates initially in the steam-poor phase, while after the main oxidation phase CO₂ is more important in molar terms under the steam-rich conditions. Methane production was insignificant (<0.02 mole injected into the containment compared with 0.64 mole of CO and 0.37 mole of CO₂). Carbon combustion, illustrated in Figure 1, reaches 77% of the total by the end of the degradation phase, and should lead to large boron release. Remarkable features are the low amounts of boron observed in relation to the carbonaceous gas transport, particularly during the first oxidation peak, in the hot leg (regulated at 700°C) downstream of the fuel bundle. In the cold leg, regulated at 150°C, the total boron that transited was only ~15% of that through the hot leg. Clearly there is large deposition of boron-containing material between the hot and cold legs, with the potential of forming a partial blockage in the circuit.

Evidence for this blockage hypothesis comes from the pressure difference observed after 14500s between the circuit hot and cold legs, Figure 3, rising to about 100mbar, and punctuated by some sharp decreases of about 40mbar around 17000s, which could be caused by partial relieving of the blockage. Further evidence comes from the strong dip in Cs transmission (on-line γ-ray data plotted in blue in Figure 2) in the cold leg from 14500s compared with the rather steady Cs transmission in the hot leg over this period; similar indications are seen for iodine and Te (not shown). Also, the character of the aerosol size...
distribution changes in the cold leg over this period; always in two populations, the population of larger sizes dominates before and that of the smaller sizes after, such as could be caused by preferential retention of larger aerosol particles in a partially blocked region.

![Figure 1: FPT3 degradation phase – B and C transport in the circuit](image1)

![Figure 2: FPT3 degradation phase - Isotopic 137Cs transport through hot & cold legs](image2)

A potential site for a blockage is in the section of the circuit hot leg approaching the steam generator hot leg (through the so-called “upstream part” where strong deposition, especially Cs has been measured, see Figure 4 that shows significant deposits there; even after leaching with water and acid, some deposition remains). In this part the temperature falls from 700°C to 150°C, with a bend in the pipe in addition, favouring deposition; one candidate is HBO2, with a melting point of 236°C [5]. One notes also the results from the previous test FPT2 [6], where a similar pressure drop about a third of the magnitude was seen, and boron was also present in the circuit (through injection into the coolant). While compounds such as caesium borate might be expected to be found in such a blockage, their fraction is unlikely to be very large as there is a big excess of boron in molar terms (order of magnitude larger).

![Figure 3: Pressure difference between the hot leg (point C) and cold leg (point G) in the FPT3 degradation phase](image3)

![Figure 4: Deposits in the upstream part of the steam generator of FPT3 after water and acid leaching](image4)

As noted in [2], the B4C also had a substantial influence on melt formation and progression, with much relocated low melting point material being found below the bottom of the heated section, contrasting with the previous test FPT2 with an Ag/In/Cd control rod where a refrozen melt pool was found in the heated section at the end of the test.

### 2.2 QUENCH

At Karlsruhe Institute of Technology (formerly FZK) the two electrically heated bundle tests QUENCH-07 [7] and QUENCH-09 [8], [9], were conducted with a B4C control rod. The bundle design with 20 heated fuel rod simulators and one central B4C control rod was very similar to that of the in-pile experiment Phebus FPT3. The QUENCH-07 bundle was heated...
Failure of the absorber rod cladding was detected at very similar temperatures in both experiments, i.e. at 1282 to 1312°C. 20% and 50%, respectively, of the B4C inventory was consumed during the two tests. In both tests the terminal injection of steam caused strong temperature escalations up to at least 2000-2200°C and significant release of hydrogen (120 and 400g, respectively). The oxidation of bare B4C and B4C-containing melts furthermore led to the formation of CO, CO2 as well as of boric acids HBO2 (meta, amu ~44) and H3BO3 (ortho, amu ~62) formed by the reaction between boron oxide B2O3 and steam. No significant amounts of methane, CH4, were detected in the off-gas. The boron-containing species were transported with the steam and were detected by mass spectrometry in the off-gas as well as by chemical analysis in the condensed water, Figure 5. Also, boric acid deposits were found in colder parts of the off-gas system.

![Figure 5: Mass spectrometer signals of boric acid species and boron concentration in the off-gas condensate taken at different times during test QUENCH-07](image)

Comparison of the results of experiment QUENCH-07 with those of QUENCH-08 without a B4C control rod but with otherwise very similar test conditions reveals the significant influence of B4C on bundle degradation, due to the formation of eutectic melts.

3 SEPARATE-EFFECTS EXPERIMENTS

3.1 BECARRE

The BECARRE program, carried out by IRSN in the framework of the International Source Term Program (ISTP) [10], is an experimental research program focused on boron carbide control rod degradation during a severe accident with core meltdown. Its objectives are to determine correlations for oxidation by steam of the B4C pellets and relocated mixtures and to improve understanding of the sequence of the phenomena involved in the degradation of B4C control rods. These correlations will allow evaluation of the quantity of gaseous by-products (hydrogen, carbonaceous gases) and to estimate their impact on the source-term.

According to sample type, BECARRE is divided into three types of tests: B4C pellets tests, B4C/stainless steel (SS) mixtures tests and B4C rod tests (in progress), see for example [11]. It was observed that when B4C pellets, Fe-5% B and Fe-6.3% B4C mixtures are exposed to steam at high temperature (respectively up to 1800°C and 1600°C), oxidation is controlled by the competition between the formation and the disappearance of a B2O3 liquid layer on the sample surface. This liquid layer acts as a diffusion barrier for the reaction. If the mixture exposed to steam is 304L SS-B4C, the B-O liquid layer formed above the surface of the
Boron evaporates from liquid layers as boric oxide and reacts with surplus steam to form volatile boric acids. Boric acids travel downstream with the outlet gases and can condense in colder parts of the facility. Condensation of boric acids has proved to be a big problem, leading to frequent blocking of the outlet circuit in B₄C-stainless steel mixture tests. Figure 6 shows H₃BO₃ deposits formed in the outlet flange of the PICCOLO facility used for mixture oxidation tests. In the 60cm-long B₄C control rod test performed at the highest temperature, noticeable quantities of B₄C were oxidised. Even if a boric acid trap were included, mass spectrometer capillaries would still be found blocked at the end of the test.

![Figure 6: H₃BO₃ deposit formed in the outlet flange of the PICCOLO facility used for oxidation of B₄C-stainless steel mixtures (internal diameter 16mm)](image)

Also observed in B₄C-stainless steel mixtures and in control rod steam oxidation tests is the projection of eutectic melts outwards from the crucible, see Figure 7, or control rod, favoured by high B₄C contents in the melt, high steam partial pressures and low temperatures.

### 3.2 Karlsruhe Institute of Technology tests

Extensive separate-effects tests were conducted at KIT (BOX, LAVA, QUENCH-SR facilities) on oxidation of pure B₄C [12], [13] as well as on the degradation and oxidation of B₄C control rods and absorber melts [14], [15]. As in BECARRE, B₄C oxidation was found to be controlled by the formation of superficial liquid boron oxide and its loss due to the reaction with surplus steam to form volatile boric acids and/or direct evaporation at temperatures above 1500°C. The overall reaction kinetics are paralinear. Linear oxidation kinetics were established soon after the initiation of oxidation under severe accident conditions. The oxidation is strongly influenced by the thermal hydraulic boundary conditions, in particular by the steam partial pressure and flow rate, and the microstructure of the B₄C.

In the configuration of typical B₄C control rods with boron carbide surrounded by stainless steel cladding and Zircaloy guide tube, rapid melt formation takes place at temperatures from 1250°C due to eutectic interactions between steel and B₄C, on the one hand, and steel and Zircaloy, on the other hand. An external zirconia layer keeps the melt within the guide tube. After failure of this protective scale at typical temperatures of about 1400°C, rapid oxidation of the absorber melts and remaining boron carbide pellets by steam takes place leading to the formation of hydrogen, and carbon and boron-containing species. As in the bundle tests, almost no methane production was detected in all the separate-effects experiments. Boric acids were formed and transported to colder test sections where they...
precipitated as can be seen in Figure 8. These processes caused blockages of the off-gas system and plugging of the mass spectrometer capillary especially in tests at temperatures above 1300°C with high reaction rates, as indicated in Figure 9. Similar obstructions were also seen for steam and argon in the same test on the same timescale.

Figure 8: Precipitations of boric acids at the outlet of the BOX facility reaction tube flange after separate-effects test on failure and oxidation of B₄C control rod segments

Figure 9: Ion currents measured at mass 62 indicating the presence of orthoboric acid H₃BO₃, with blockage formation increasing after 1000s (BOX facility)

Oxidation of pseudo-binary and ternary B₄C-SS-Zry melts in steam is significantly faster than that of the solids. Experiments with prefabricated eutectic compositions showed a rapid increase of oxidation rates at melting temperature. Furthermore, it was shown that 1wt.% boron carbide is able to liquefy 99 wt.% steel at temperatures around 1220°C, i.e. 200 K below the melting temperature of steel.

4 DISCUSSION

The experiments summarised above show remarkably consistent results as regards oxidation of B₄C control rod material in steam under severe accident conditions and transport of boron-containing material in the offgas line/primary circuit. Firstly, there is general agreement as to the mechanism of oxidation and regarding the reaction products (initially boric oxide, then boric acids according to the amount of steam present and the temperature conditions, cooling along the circuit line, along with CO and CO₂ formation, but negligible methane). Blockages due to boric acid-containing materials have been seen in all the tests summarised, specifically in Phebus FPT3 where its presence significantly reduced the transport, at certain times, of volatile fission products such as Cs and I towards the containment; this behaviour needs to be taken into account in the interpretation of the results. What will need to be analysed further is the prototypicality of such results; would similar partial blockage(s) occur in-reactor and where; a first step could be to see if current transport codes can predict the blockage seen in FPT3, and if the predicted speciation in the circuit is consistent with such data that are found. It is clear, however, that blockage effects are plainly observed on the experimental scale; note for example how the blockage seen in FPT3 occurs under a similar timescale to that seen in the small-scale test at KIT illustrated in Figure 9.

Secondly, while this paper focuses mainly on circuit phenomena, it is worth recalling the effect of B₄C-containing control rods in accelerating core degradation, connected with B₄C-stainless steel (SS) eutectics formation and liquid B₄C-SS-Zry relocation, including spreading of such aggressive melts towards neighbouring fuel rods, which are attacked and degrade early, well below the Zircaloy melting point of 1860°C (note that pre-existing ZrO₂ films may retard this effect [16]). This could cause early release of fuel and fission products. This accelerated degradation has been shown in many earlier integral experiments such as

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5 CONCLUSIONS

Recent integral and separate-effects tests at IRSN Cadarache and Karlsruhe Institute of Technology relevant to oxidation and degradation of B₄C control rods under severe accident conditions have been compared. The integral Phebus FPT3 and QUENCH experiments reinforce the existing database regarding the accelerated degradation of fuel rods due to spreading of chemically aggressive eutectic melts from failed B₄C control rods onto neighbouring fuel rods, which could lead to early release of volatile fission products, while the separate-effects tests give quantitative data that could be used for development of detailed material interaction and oxidation models. The integral tests agreed that methane formation under the experimental conditions used was negligible. There is also agreement on the formation and transmission of boron compounds (boric oxide, boric acids) under hot leg conditions typical of a severe accident, with blockage formation, in regions of strongly decreasing temperature, which can reduce the transport of volatile fission products. The results should be compared with the results of current severe accident analysis codes, and model improvements made if necessary, taking into account plant safety analysis needs. The upcoming benchmark exercise on FPT3 in SARNET2 will be a good basis for such activity.

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