Enhanced Safety Margins During Wet Transport of Irradiated Fuel by Catalytic Recombination of Radiolysis Hydrogen and Oxygen

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BNFL has developed and tested a new method for use in wet transport of irradiated fuel. The method uses a catalyst to recombine the hydrogen and oxygen produced from radiolysis. The catalyst is installed in the nitrogen ullage gas region. It has twin benefits as it eliminates a gas mixture that could, in principle, exceed the safe target levels set to ensure safety during Transport, and it also reduces overall gas pressure.

Pure water radiolysis predictions, from experiment and theory, indicate very low levels of hydrogen and oxygen generation. BNFL's historic experience is that in some transport packages it is possible to produce higher levels of hydrogen and oxygen. This drives the need to improve on our existing ullage gas remediation technology. Our studies of the radiolysis science and our flask data suggest it is the interaction of the liquors and material surfaces that is giving rise to the enhanced levels of hydrogen and/or oxygen.

This technical paper demonstrates the performance of the recombiner catalyst under normal and extreme conditions of transport. The paper will present experimental data that shows the recombiner catalyst working to manage the hydrogen and oxygen levels.

Introduction

BNFL routinely ship irradiated fuel in water. The fuel is carried in a multi-element bottle (MEB) which is used only once and shipped in a re-useable outer shielded flasks. A list of some of the current combination is shown in Table 1 below. An example combination is shown in Figure 1.

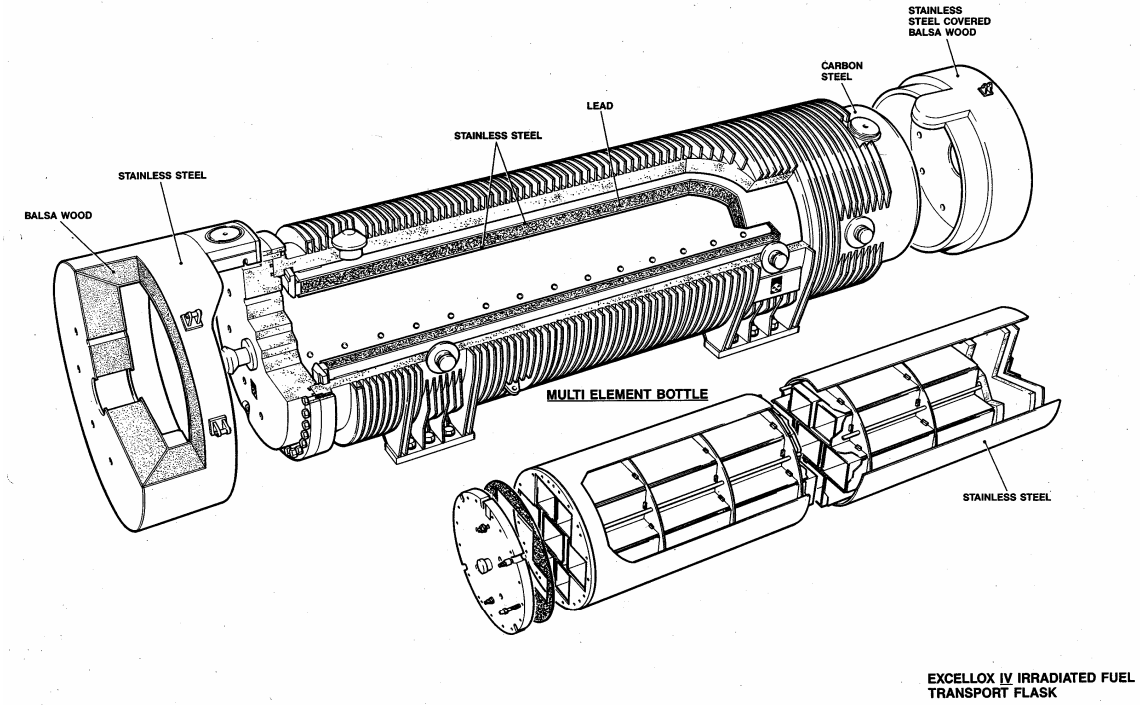
Outer package or flask	MEB Inner package	Example Utility
Excellox 6	Type 3349	Neckarwestheim,
	Type 4450 or 4451	Emsland/Broksdorf
NTL11	Type 3346	Beznau
	Type 3184	Krummel
Castor S1	Type 3328	Unterweser
NTL3MA	Type 3327	Garigliano

Table 1: Flask and MEB combination

One consequence of wet transport is that the gamma and neutron radiation from the fuel will generate hydrogen and oxygen gas by radiolysis. The precise mechanism by which the hydrogen and oxygen is generated is discussed briefly towards the end of the paper.

Historic levels of hydrogen and oxygen were generally low in MEBs. BNFL's design of these has evolved over the last twenty-five years. The internal framework was originally stainless steel with boronated aluminium (Boral) plate-shaped spacers as neutron absorbers to reduce the reactivity (k-effective) of the fuel. The design of the internal fuel separator framework evolved with the move to boronated stainless steel. A secondary function for the Boral had been identified in that the material corroded and acted as an oxygen getter. This eliminates any excess oxygen produced from radiolysis inside the MEB. Boral sheets were retained inside the boronated steel MEBs with the same active surface area available to corrode and still act as an oxygen getter even though the need for criticality safety had been eliminated since adequate boron was now in the stainless steel framework. During the early 1990s gas sample data results from MEBs showed some inconsistencies, in particular. Some flasks came back with relatively high hydrogen and oxygen levels.

Figure 1 An Excellox 4 outer flask and a corresponding Multi Element Bottle (MEB)



EXCELLOX IV IRRADIATED FUEL TRANSPORT FLASK

The extra radiolysis hydrogen and oxygen has two main consequences:

1) It adds a small amount extra to the internal pressure in the ullage gas. The function of ullage gas is to provide a pressure relief mechanism as the heated water expands inside the MEB. The gas is compressible, but adding extra molecules of hydrogen and oxygen will slightly erode the large safety margin.
2) Secondly, some mixtures of hydrogen and oxygen are potentially flammable or explosive. Extensive studies have shown there is minimal chance of ignition in the MEB. It is known that the auto-ignition temperature for hydrogen oxygen mixtures is higher than 540°C. Furthermore experimental work has shown that the metal to metal contact points present inside a typical MEB do not generate conditions which are ever hot enough or exist for long enough to ever initiate combustion.

Despite this minimal risk it was thought worthwhile by BNFL to explore the possibility of identifying and testing a gaseous phase catalyst to insert into the MEB to eliminate any hydrogen and oxygen build-up. BNFL historically have had experience of using catalysts to remove hydrogen and oxygen in containers of AGR fuel stored in ponds at Sellafield. The research programme has taken 7-8 years to be completed. This aim of this summary paper is to describe the key features of the development and testing of the catalyst we have adopted.

The remainder of the paper breaks up into the following sections:

- A brief discussion of the target hydrogen and oxygen levels;
- A description of the experimental test set-up and methodology;
- A review of the key performance characteristics and the test results;
- A discussion of how the results may have an impact on the underlying science of radiolysis;
- A summary of the conclusions which can be drawn from this work.

Target Hydrogen and Oxygen Levels

The target levels for H_2 and O_2, which BNFL aim to achieve were based on the design guide[1]. The relevant section of which is summarised below.

In line with best industrial practice for vessels, the objective for the design of any new transport or storage container should be to limit the average concentration of hydrogen in air, in any part of such containers, to less than 1% during normal operations irrespective of the oxygen concentration. Alternatively the limit should be to keep the oxygen level below 2% irrespective of the hydrogen concentration.

These target limits are based on the Lower Flammable Limit (LFL) of 4% hydrogen in air and the Limiting Oxygen Content (LOC) of 5% below which combustion cannot occur. The guide sets a target to step back from LFL and LOC to the levels of 1% hydrogen or 2% for oxygen to be in line with the best industrial practice. It should be noted that combustion is barely sustainable at the LFL and LOC hydrogen/oxygen levels.

The design guide indicates that the minimum explosive limit in air is at least 8.5% H_2 in air. In addition if the oxygen levels are lower than in air (i.e. <20% O_2), as in our MEBs which are ullaged with 100% nitrogen, then the minimum explosive hydrogen concentration will be higher than 8.5%.

Experimental Test Programme

A pilot-scale MEB rig comprised of a short section 1/6th the length of a full-size MEB container (illustrated in Figure 2) was used to test the catalyst performance of the two catalyst materials. The 600L vessel is filled with approximately 500L of boric acid ($B(OH)_3$, 11,300 ppm), leaving a gas space (ullage) of approximately 100L. The temperature of the boric acid solution in the MEB was controlled by means of an electrical heater thermostatically controlled to give a range of 35-150°C.

Figure 2. MEB Testing Rig.

The catalyst material was loaded into a perforated stainless steel catalyst holder. The holder was then attached to a crankshaft on the lid of the MEB vessel and the lid secured to the body of the vessel. An actuator attached to the crankshaft handle was employed to transfer the loaded catalyst holder between the ullage and the boric acid solution in order to simulate repeated splashing.

The experimental method used to test the catalyst in the mini MEB vessel is summarised as follows. The ullage of the pressure vessel was initially purged with either high purity nitrogen (low temperature experiments) or steam (high temperature experiments) to remove any air or residual gas from the previous experiment. Depending on the type of experiment, the loaded catalyst holder was then transferred either to the gas phase (undipped catalyst run) or the liquid phase (dipped catalyst run). The gas reservoir was then charged to the desired pressure (8-21 bar) with reagent gas. At time zero, the reagent gas in the reservoir was then introduced into the ullage of the pressure vessel. Samples of the ullage were then taken at 2-4 minute intervals over a period of about 120 mins and analysed for hydrogen using gas chromatography (GC). The actuator on the crank handle was used to immerse and remove the catalyst from the boric acid solution periodically.

Three different types of tests were performed in the mini MEB recombination rig.

- Undipped catalyst trials: catalyst remains in the ullage for the entire duration of the catalytic run.
- Single dip catalyst trials: catalyst is immersed in boric acid and subsequently removed from solution 30 mins after injection of reagent gas in order to assess the efficiency of drainage in response to wetting.

- Multiple dip catalyst trials: catalyst is immersed in boric acid and subsequently removed from solution 30 mins after injection of reagent gas. The catalyst is then lowered into the solution and raised into the ullage alternatively at 15 second intervals to simulate the effect of frequent splashing as might take place during transport of an MEB by sea.

Experiments trials were carried out at 35°C, 75°C and 150°C respectively.

The catalyst will immediately begin to convert H_2 and O_2 into H_2O when introduced into the ullage containing the reagent gas, resulting in a gradual decline in the H_2 concentration, with time. This can be followed by GC as shown in Figure 3. The decline can normally be made to fit the following equation for a first order reaction:

$$c = c_0 e^{-kt} \qquad \text{(equation 1)}$$

Where: c = concentration of hydrogen (% v/v);
c_0 = concentration of hydrogen in the ullage immediately after injection;
k = rate constant (min^{-1});
t = time elapsed since injection of gas (min).

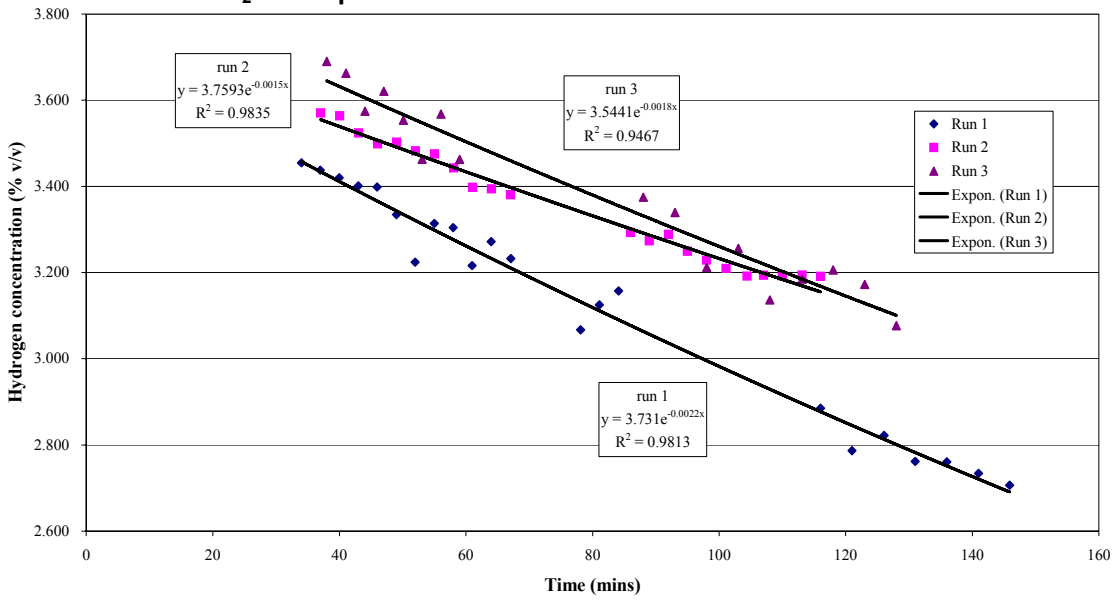
The rate of recombination is therefore directly proportional to the concentration of hydrogen. A plot of hydrogen concentration, c, versus time, t, therefore yields an exponential trend line and the rate constant, k, can be obtained from the gradient. The rate constant can then be converted into a more useful value, referred to as Reactivity, R (L day^{-1} $\%^{-1}$) by expressing the hydrogen concentration as a volume fraction and multiplying by the volume of nitrogen in the pressure vessel at room temperature and pressure (RTP).

$$R = k \times 1440 \text{ (min/day)} \times V(N_2) / 100\%; \qquad \text{(equation 2)}$$

In MEBs there are other effects and reactions, degradation of any organic material in the water, corrosion of Boral, and out-gassing of water which can change the air concentration in the ullage gas. In all the laboratory trials, however, it is the hydrogen level, which is more conveniently measured, as there are no competing corrosion reactions to interfere.

Catalysts would be exposed to gaseous mixtures arising as a result of the radiolytic breakdown of water, i.e. stoichiometric quantities of H_2 and O_2 in a ratio of 2:1. Therefore, tests were carried out using a gas mixture comprised of 4%H_2, 2%O_2 and 94%N_2, which is similar to the gas composition of the MEB ullage and initial concentrations at the upper bound of the flammable safety limit.

Figure 3: Data Obtained During Multiple-Dip Tests at 150°C on catalyst irradiated with 21MGy of gamma radiation under an N_2 atmosphere.



Catalyst performance

The series of experiments have taken 3-4 years to complete. It is impossible to summarise all the details here in a short paper. Instead the key performance characteristics are briefly reviewed.

Effect of temperature

Sets of experimental tests were carried out with the MEB water and ullage gas at three main temperatures:

- 35°C to represent typical room or storage pond temperatures;
- 75°C to represent a upper-bound normal condition for a full fuel load being transported from the reactor to BNFL Sellafield;
- 150°C to simulate an extreme heat load of > 20kW in an MEB. This is a worst case and unlikely to occur in practice as most fuel thermal heat-loads are much less.

The trials showed that the lowest recombiner reactivity occurred at the lower temperature of 35°C. It is thought that this occurred since at lower temperatures it takes slightly longer to shed the water from the catalyst.

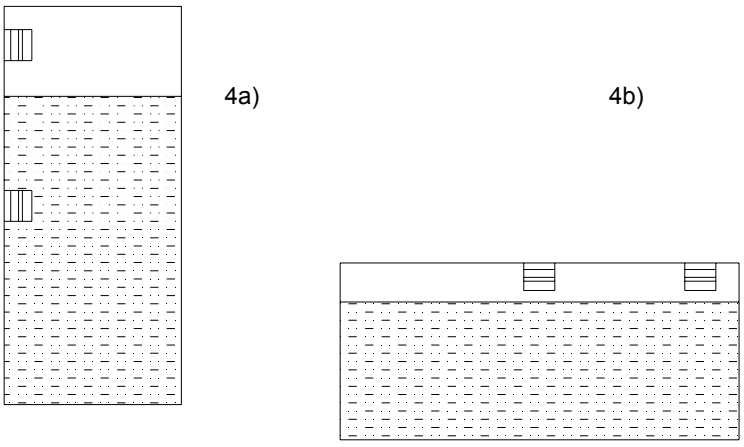
Hydrophobic nature of Catalyst

The catalyst was chosen because of its known ability to shed water quickly and effectively. The rapid time to shed water is illustrated by the multi-dip experimental trials. In these the catalyst is plunged into the MEB liquor every 15 seconds, removed into the ullage gas for 15 second and the process then repeated for many hours. The time take to shed water has to be tiny otherwise the catalysis observed during the multi-dip trials would be negligible, experimentally the hydrogen recombination ability is clearly not negligible.

Effect of splashing

The catalyst is clearly hydrophobic so that during sea shipments (and to a much lesser extent during rail or road transport) the catalyst will shed water and continue to work. To minimise the effects of water splashing the operational implementation of catalytic recombiners involves installing two groups of catalysts as shown in Figure 4. This strategy is probably unnecessary as the fuel and steel framework act as baffles that will greatly attenuate water sloshing during transport. Given that it is straightforward to engineer the catalyst is installed with half at the top and available for use for the short periods of time when the MEB is stored loaded, ulllaged and vertical. In the normal horizontal orientation the other batch of 50% of the catalyst at the centre of the flask is also now in the ullage space and available to recombine hydrogen and oxygen.

Figure 4: Schematic showing holder location in an MEB is above the liquor level in a) vertical and b) horizontal orientation



Effect of Radiation

If catalyst was irradiated for a whole year in an MEB the maximum possible dose for estimated as 42 MGray. This was based on a high burn-up and short-cooled fuel load and pessimistic calculations with the computer codes FISPIN to calculate the reactor inventory and McBend to determine the radiation levels in the ullage region where the recombiner catalysts will be installed. To simulate this eventuality two samples of catalyst were irradiated at the Petten Institute in Holland, one with 42 MGy and a second with 21MGy. The samples were irradiated with gamma radiation as this dominates the radiation exposure. This dose value is grossly pessimistic as a typical European

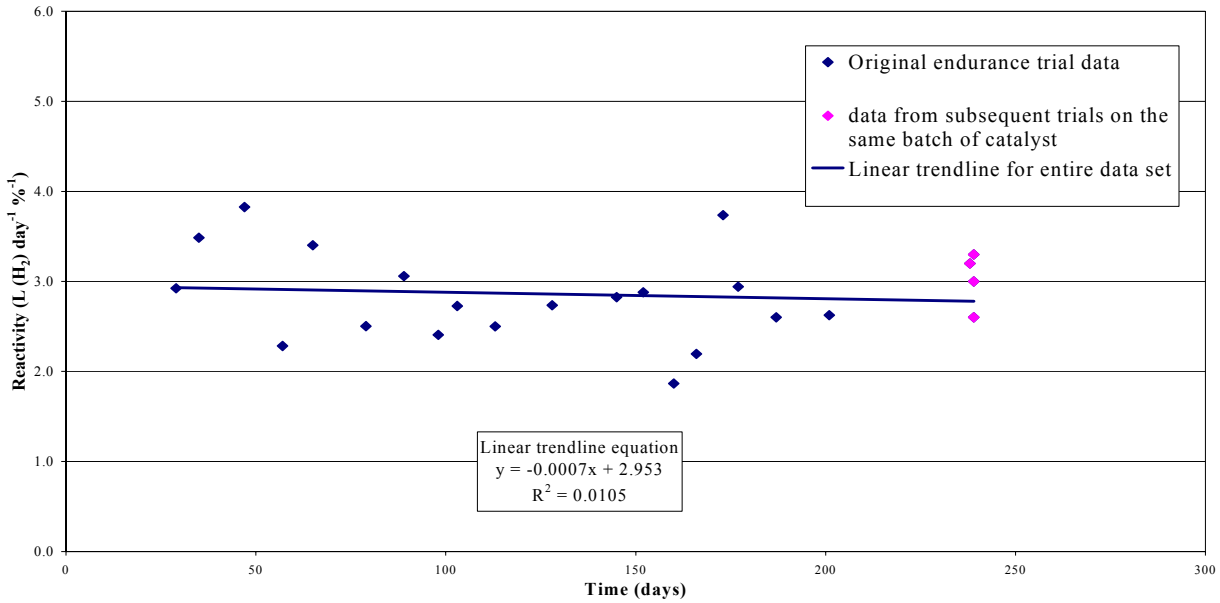
fuel shipment takes 40 to 50 days so that the hydrogen catalyst rarely sees more than 15-20% of the assumed worst case radiation dose.

Does the Catalyst Performance Change with Time

To confirm that the catalyst did not degrade over time during service one of the two mini-MEBs was set-up to complete a long-term performance trial. The MEB was maintained at 150°C for the whole period and regular single-dip trials of the catalyst performance were initiated. The results are shown graphically in Figure 5.

It can be seen that the reactivity of the sample is essentially constant over the period of 250 days. There is some statistical scatter on the data arising from the various experimental uncertainties, it is clear, however, that over a period of one year that the performance of the catalyst can be assumed to be constant.

Figure 5:Reactivity value as a function of time for single dip experiments at 150°C with catalyst irradiated with 42MGy of gamma radiation/N_2 tested in the mini MEB rig.



Demonstration of Catalyst Performance in an MEB in a Sellafield Cooling Pond

The final test of the performance of the catalyst was to open an MEB, load two catalyst holders inside, replace the MEB lid, add ulllage gas to the MEB again with a nitrogen atmosphere again and replace in the THORP cooling pond. The MEB was then recovered at regular intervals and samples of the ullage gas taken and analysed in a separate off-line mass spectrometer.

The gas analysis of the MEB when it arrived from the utility showed the ullage contained and thus before the catalyst recombiners were fitted are shown in Table 2. Composition figures for the same flask after the inclusion of the recombiner assemblies are shown in Table 3. Note sampling has to stop when the ullage pressure becomes too low to take another sample. This and the data for a second MEB both showed that the levels of oxygen and hydrogen have reduced with time.

It is noticeable that the oxygen level initially increases but then falls down to near zero. After gathering and reviewing gas analysis data over 43 shipments this is now better understood. Radiolysis hydrogen is recombined quickly as there is an excessive of catalyst fitted in the MEB. There is still some hydrogen being produced within the MEB from corrosion for the Boral. No oxygen arises as it is fixed in the corrosion products. There is however some oxygen released into the ullage gas as there is dissolved oxygen in the pond water which out-gasses into the ullage gas to satisfy the Henry's Law equilibrium. This out-gassing oxygen is gradually consumed with the corrosion generated hydrogen, so that ultimately the oxygen is exhausted and tends to zero, leaving a small excess of hydrogen. It is expected that there will always be a small residual level of hydrogen or oxygen as the gas transfer is dependent on diffusion and convection currents to mix the gas.

Table 2: Gas Sample Data on receipt at Sellafield Pond

MEB Number	Sample Date	Time fuel has spent in MEB (days)	Pressure in MEB (bara)	H_2%	O_2%	N_2/CO%
3349/1715	18/05/01	87	3.6	17.65	8.02	74.12

Table 3: Gas Sample Data from 3349/1715 with Recombiner Assemblies Fitted

Lab sample No	DATE	Pressure (bara)	Days Ullaged	H_2 %	N_2+CO %	O_2 %
712513	05/10/01	1.4	0	1.21	98.25	0.51
714966	19/10/01	1.35	14	0.097	98.87	0.75
717475	02/11/01	1.30	28	0.099	99	0.59
725843	14/12/01	1.30	70	0.22	99.37	0.08
748146	12/04/02	1.10	189	2.66	96.87	0.08

These results confirm that the recombiners work under full-scale active conditions in an MEB and that the limiting concentrations of hydrogen and oxygen recommended for normal operations are not exceeded as the oxygen level is maintained well below the target level of 2%.

Uncertainty in the Mechanism of Radiolysis

BNFL's understanding of the science of water radiolysis has been improved following this experimental research programme. The original plant measurements showed that under some circumstances that the yield of H_2/O_2 from the traditional semi-empirical "G" value approach was difficult to extrapolate to new situations.

Theoretical model predictions of H_2/O_2 yield based on modelling all the complex chain reaction in the liquor significantly underestimated the volume of hydrogen produced in a typical transport flask. This contradicted the empirical H_2/O_2 data. Clearly some factor in MEBs and liquor enhanced the H_2/O_2 yield.

From recent academic research, it has been shown that the quantity of hydrogen generated is increased due to a process called 'radiocatalysis'. Radiocatalysis is a process whereby the quantity of hydrogen generated through water radiolysis is increased in the presence of certain photo-active materials[2], such as zirconia, which is commonly found in fuel assemblies [2]. Radiation causes water to breakdown at the surface of these materials, in a process, which is essentially catalytic. The radiocatalytic enhancement of water radiolysis has lead to a re-assessment of the fundamental process by which hydrogen gas is formed during water radiolysis [3].

It turns out, that BNFL's approach to controlling hydrogen is in effect using catalysis to control a phenomena resulting from a catalytic generation process. This research will ultimately allow us to better predict the quantities of hydrogen arising during the transport of spent fuel, and in other radioactive scenarios. It is also possible to consume oxygen during organic material degradation or generate hydrogen from corrosion.

Discussion

In summary of results the catalyst has been shown to work:
1) At a full range of temperatures which might arise in practise;
2) The effect of repeated (for 50% of the time) immersion in water has been measured and allowed for.
3) The effect of a worst case radiation dose has been quantified and allowed for.
4) The catalyst has been show to work in an MEB in a pond trial.

Table 4 show typical data sets from gas sample analysis of MEB ullage gas on arrival at Sellafield confirming that the recombiner catalyst is working effectively. The results show that either the hydrogen or oxygen levels are effectively reduced to zero as the catalyst is so effective at consuming any excess H_2 or O_2. The excess hydrogen in the Neckarwestheim case is from Boral getter corrosion. In the Garigliano case the Boral getter have been omitted, so the excess hydrogen from Boral corrosion is not observed. The slight excess of oxygen results, we

believe from slow out-gassing of the dissolved oxygen into the ullage. The net excess of oxygen remains as no "corrosion" hydrogen is generated to combine with it.

Table 4: Three typical ullage gas analysis results for MEBs shipped recently with catalytic recombiners.

Reactor Station	MEB Type/ MEB id Number	Sample Date	Days fuel spent in MEB	Pressure in MEB (bara)	H_2%	O_2%	N_2/CO %	CO_2 %	Ar%	Comments
Neckarwe sthiem	3349/1831	20/02/04	34	1.25	6.45	0.01	92.56	0.89	0.096	Safe as O_2 < 2%
Neckarwe sthiem	3349/1832	20/02/04	38	1.2	2.75	0.00	96.58	0.57	0.1	Safe as O_2 < 2%
Garigliano	3327/1789	30/01/04	46	1.15	0.043	2.6	97.17	0.03	0.16	Safe as H_2 < 1%

Conclusions

Based on the extensive laboratory tests over 4-5 years the recombiner catalyst solution was adopted for MEBs used by BNFL to ship irradiated fuel within European from 1st January 2003. Since that date more than 42 shipments have occurred all with levels of hydrogen or oxygen safely below the target safe levels showing that the potential risk has been eliminated.

References

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3. M. Bankhead "*Theoretical study of excited states, hydrated electrons and water radiolysis*." In preparation.

Acknowledgements

This study could not have been completed without major contributions from Ramon Gater, Ashley Pugh, Manon Higgins-Bos and Robin Jones.