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FUEL, MATERIALS AND COOLANTS FOR WR-1

by

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SUMMARY

Pressed and sintered UO_2 is well known as a fuel for water cooled and moderated reactors. In WR-1 however there is a combination of UO_2 fuel sheathed in zirconium alloys, cooled by an organic fluid flowing in a zirconium alloy pressure tube which is unique in nuclear reactor experience. The behaviour of this system to date will be described.

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1. INTRODUCTION

The WR-1 reactor is unique not only in Canada but also in the world today. In two other papers presented to this conference (1,2) it has been pointed out that it is a heavy-water-moderated pressure-tube type of reactor fuelled with UO_2 and cooled with an organic liquid. No other reactor either in the Western or in the Eastern world is operating with the combination of moderator, coolant, fuel and materials found in WR-1. The particular combinations chosen or under test have evolved from some very interesting development studies over the past few years. This paper will review briefly, and of necessity rather generally, some of the work leading to the particular choices of coolant, materials and fuels found in WR-1 today.

The reasons for the choice of an organic liquid as a nuclear reactor coolant have been discussed elsewhere (3,4) as has the course of Canada's organic-cooled reactor program (5). No further elaboration will be given here. The work described in this paper, which culminates in the present reactor, has been the result of the cooperative effort of many people, not only in AECL but also in Canadian industry, especially Canadian General Electric. In this presentation not all published work will be acknowledged and indeed the work of many who were vitally instrumental in bringing the reactor to its present state of efficiency does not appear in the published literature. However in this paper I would like to acknowledge the assistance of all those who participated in the design, development, construction, commissioning and operation of the reactor.

2. COOLANT

The coolant originally chosen for WR-1, and indeed the present "reference" coolant, is based on a commercial mixture of terphenyl isomers marketed by the Monsanto Company under the trade name of Santowax OM. This mixture is a solid at room temperature with a melting point of 85°C. However under irradiation the main products are higher molecular weight polymers of high boiling point and are called High Boilers (HB) as a class. It has been found that if HB are allowed to build in to 30 wt. percent, the resulting mixture is a viscous, probably supercooled, fluid at room temperature. It has the consistency of heavy molasses, but it can be pumped in a circuit at room temperature and the process system using it needs a minimum of trace heating. The mixture of Santowax OM + 30% HB has been successfully used as coolant for in-reactor loops at CRNL. In this instance the HB were those separated from the OMRE reactor in the U.S.A. and were mechanically mixed with the Santowax OM prior to irradiation.

For its use in a reactor however, problems arise. In the WR-1 type of reactor the coolant must flow past the fuel in very narrow channels; hence, a low viscosity is mandatory. Santowax OM is a solid at room temperature; considerable trace heating would be necessary, thus increasing the capital cost. The problem of trace heating the coolant channels is particularly difficult especially since the presence of parasitic neutron absorbers must be minimized. HB from another reactor could be used to lower the melting point and this process is indeed feasible. This would mean, in effect, adding reject material from one reactor into another; special melting and mixing equipment would also be necessary. Considerable purification, probably by distillation of the HB fraction, might be necessary especially if it had become contaminated in any way.

Thus it appeared quite early in our investigations that a most attractive goal would be to produce an alternative coolant, which had about the same physical and chemical properties as Santowax OM but which was a liquid at room temperature. In practice, lower thermal and radiolytic stability could be accepted if this material were only used as a start-up coolant and were gradually replaced by Santowax OM, by a feed-and-bleed system as HB built up.

In 1962 a search was started and several alternatives were considered (6). One of these was HB-40, a partially hydrogenated terphenyl which was commercially marketed by Monsanto Company. This material, which has an acceptable viscosity of about 14 centipoise at room temperature, is used as a heat transfer fluid but its main use is in the plastics industry as a plasticizer. Some earlier screening work in the U.S.A. had indicated that the thermal and radiolytic stability of HB-40 were markedly inferior to that of Santowax OM. However it was a commercially available mixture, whereas the other alternatives tested in the early experiments were not, and for completeness it was included with our initial tests. The relationship of HB-40 to Santowax OM is illustrated in Fig. 1.

Rather to our surprise, HB-40 passed these tests remarkably well, one reason being that the dosimetry was better known than it had been previously (6). Of the four materials tested it did indeed show the poorest thermal and radiolytic stability, but the decomposition rates were low enough that it looked attractive, at least as a start up coolant. The leading contender, a eutectic mixture of ortho and meta terphenyl and biphenyl was liquid at room temperature only if the para-terphenyl content could be controlled at less than 2 wt. percent. Monsanto indicated that this was feasible, but only at a price that was not at all attractive. The other contender, a partially hydrogenated mixture of ortho and meta terphenyl, was in a very embryonic stage of development and a product free from crystals at room temperature could not be guaranteed.

Thus our alternative at that time was either to spend quite large sums of money on further development or to test HB-40 in a more detailed and exhaustive manner. We chose the latter alternative. Testing continued in capsules in the NRX reactor and in association with our Van de Graaff electron accelerator at Whiteshell. More important, a small loop, the E-2 loop, was built for use in NRX in which the coolant could be recirculated at temperatures up to 400^{0}C and experiments could be performed under steady state conditions. The mixed radiation flux found in the test section of this experiment was a close approximation to that in the WR-1 reactor (7). Table I shows a comparison of the physical properties of Santowax OM and HB-40 while Table II illustrates comparative decomposition rates obtained in the E-2 loop.

TABLE I

COMPARISON OF SANTOWAX OM AND HB-40

	Santowax OM	Santowax OM + 30% HB	HB-40	HB-40 + 30% HB
Final Melting Point ^{0}C	85	67	<0	<0
Vapour Pressure (lb/in^{2} abs)				
at 350^{0}C	16	14	19	20 - 50 (a)
at 400^{0}C	40	34	39	40 - 95 (a)
Viscosity (cP)				
50^{0}C	27	1000	14	$\sim$100
350^{0}C	0.23	0.47	0.29	0.47
Density (g/cm^{3})				
50^{0}C	1.07	1.10	0.99	1.02
350^{0}C	0.82	0.87	0.76	0.80

(a) Range is indicated. Actual value depends on degassing rate which determines the concentration of low boiling constituents.

TABLE II

COMPARISON OF STEADY-STATE DECOMPOSITION RATES (a,b)
AT 350^{0}C

	Santowax OM	HB-40
HB content (wt. %)	33	33
Gas formation rate	<0.2	0.7
Volatiles formation rate	0.0	2.4
"HB" formation rate	16.5	15.0
Total coolant consumption rate	16.5	18.1

(a) Rates measured as grams produced (or consumed) per kilowatt-hour of radiation energy absorbed in coolant.

(b) Experiments performed in E-2 loop in NRX. Dose rate in test section $\sim$0.3 W/g. 62% of absorbed dose due to fast neutron interactions, remainder due to γ-ray interactions.

Development has continued to be encouraging, and the present status may be summarized as follows:

(a) Overall decomposition rates are not significantly higher for HB-40 than they are for Santowax OM(8). Gases and volatile components boiling in the range of benzene are indeed produced at many times the rate they are in Santowax OM. However the absolute rate is reasonable and gas and volatile concentrations in the coolant system can be controlled by use of the degassing circuit. There is evidence that if volatiles are not stripped out initially they enter further into radiolytic reactions to form higher molecular-weight and higher boiling-point compounds, some of which appear to be useful coolant.

High boilers are produced at a rate somewhat higher than their production rate in Santowax OM. However they are less thermally stable, and at temperatures of 300^{0}C and above, and certainly at the temperatures of the distillation unit (350 - 400^{0}C), they "crack" to lower molecular-weight products. Again these products, which may not be the original compounds found in HB-40, appear to be useful coolant. Thus the net HB formation rate is about the same and the more important parameter, that of the actual coolant consumption rate, appears to be not significantly higher in HB-40 than in Santowax OM.

(b) The fouling potential of HB-40 under irradiation does not appear to be any higher than that of Santowax OM as long as similar precautions are taken (9). These include exclusion of chlorine and oxygen from the system and control of the water content in the range 100 - 200 ppm. We have been operating the X-7 loop in NRX using HB-40 as coolant for the past year, at temperatures as high as 370^{0}C. In this loop we have also had Zr-Nb and SAP clad UO_2 fuel specimens operating at the maximum ratings expected in WR-1 ($\sim$100 W/cm) and have seen no evidence of fouling beyond what would be expected from Santowax OM. Comparative experiments in a small loop in conjunction with our Van de Graaff accelerator have also shown no demonstrable difference between the two coolants.

By the end of 1964 the decision was made that the WR-1 reactor should be started up using HB-40 as the start-up coolant. Santowax OM remains as the reference equilibrium coolant, and our present plans call for gradual replacement of the HB-40 by Santowax OM when the HB content has reached 30% and steady-state conditions have been achieved. This decision may be reviewed if HB-40 shows adequate high-temperature properties and an adequately low fouling potential. In such an event we may well leave HB-40 as coolant in at least one of the two reactor circuits.

Coolant behaviour to date has been very encouraging in the WR-1 reactor. Our decision to use a low-melting coolant as a start-up fluid has been amply justified. We are now operating the reactor at a coolant outlet temperature of 350^{0}C. Decomposition rates appear to be those preducted. Fouling potential as measured by special probes, although higher than desirable, at 2 to 4 $\mu g/cm^2$-h, is no higher than we would expect with Santowax OM. There does not appear to be any problem in keeping chlorine, oxygen and ash concentrations at the required low level and a water control at 150 ± 50 ppm is readily achieved.

We still have much to learn about the operation of organic coolants at high temperatures in a nuclear reactor. Continued operation in WR-1 will do much to fill in many of the gaps in our knowledge. For instance our knowledge of the fouling problem is still embryonic and we do not really know the optimum methods of reducing and controlling the fouling potential of the coolant. One experiment now underway is to determine whether continous purification by the use of Attapulgus clay columns is really necessary. We are operating one coolant circuit with clay columns and the other without. To date there are indications that while the clay may be very useful in cleaning badly-contaminated coolant, it is really not much use during operation with clean coolant.

3. MATERIALS

We are testing fuel clad in SAP (Sintered Aluminum Product), a material consisting of Al + 10% Al_2O_3 prepared by a powder metallurgy process. However, in Canada today there is not an active SAP development program, although much work is being done both in the U.S.A. and at Euratom. We are completing our irradiation test work to round out the Canadian contribution to this technology (10). Poor performance of SAP in early irradiations indicated that we should search for an alternate cladding and pressure-tube material. Because zirconium alloys had performed well in water-cooled reactors they were an obvious choice.

Early exploratory work in the U.S.A. indicated that zirconium alloys were unattractive in organic coolants at high temperatures because they hydrided, embrittled and fell to pieces in a matter of hours in this environment. However, by 1960 the X-7 loop was operating in NRX at CRNL and the opportunity was taken to insert some zirconium alloy corrosion specimens in the coolant. These resisted attack surprisingly well and as a result, we started giving serious thought to the use of zirconium alloys. There is not time or space to give the details here, but we found that these alloys could indeed be used in organic coolants if certain precautions were taken. Nature has been kind to us in that we have found that two of the important variables affecting fouling, i.e. chlorine and water, also have a significant effect on the oxidation and hydriding of zirconium alloys (11).

Traces of chlorine, as low as 2 ppm, can affect hydriding very adversely, especially when the chlorine occurs as compounds such as HCl or trichlorethylene, which undoubtedly dissociates to HCl. Thus in WR-1 we have stringent regulations regarding the use of chlorinated solvents; there is a maximum specification of 2 ppm on feed coolant and we have available, for use when required, a catalyst of Pd on Al_2O_3, which is effective as a chlorine remover. To date we have had no difficulty in maintaining chlorine contents of less than 0.5 ppm.

The presence of water has been found to be very necessary to retain the protection offered by the ZrO_2 film. Whether the water is required to heal cracks or replace ZrO_2 lost by dissolution in the metal is not yet known. The presence of 100 ppm of water in the coolant is necessary to maintain a coherent ZrO_2 film which acts as a barrier against the ingress of H_2 from the coolant to the metal. Under these conditions we have been able to show that the nature of the organic coolant is not important in that it acts only as a carrier, and that corrosion and hydriding rates are just those one would expect in steam at the same temperature and partial pressure. Thus as long as chlorine is absent and 100 ppm water is present one should expect zirconium alloys to behave the same in either Santowax OM or HB-40. This has been shown to be the case.

The two most effective alloys to date have proven to be Zircaloy-4 and Zirconium 2.5 wt. % Nb. Our present data on hydriding rates are shown in Fig. 2. These data do not include an allowance for the effect of irradiation. At 480^0C where annealing rates are rapid there is probably no effect but at temperatures of 400^0C or less the rates shown may be low by a factor of two or three.

In WR-1 the fuel charge is clad in Zr-2.5 Nb alloy and we have four experimental pressure tubes, two of Zircaloy-4 and two of Zr-2.5 Nb, under irradiation. There are also zirconium alloy corrosion specimens attached to the hanger rods of fuel strings in the zirconium alloy pressure tubes. It is too early to obtain any experimental data from these assemblies, but referring to Fig. 2, we can forecast some lifetimes based on the criterion that once the terminal solubility of ZrH_2 is reached in the cladding or in the pressure tube, then the useful life of the assembly is ended. I will not discuss here whether or not this is a good criterion, but on this basis we can predict a useful life of the fuel sheaths of 1½ years and of the pressure tubes of 5 years (11,12). The calculation of these lifetimes has included a factor assuming an increased corrosion rate under irradiation. We feel that they are probably pessimistic; however, better data will come from the operation of WR-1 itself.

In a large organic-cooled power reactor the desirable lifetime of the fuel is probably 3 years and of the pressure tubes at least 15 and preferably 20 years. Obviously zirconium alloys with lower corrosion and hydriding rates would be attractive. We are now looking at two promising alloys which are potential candidates for high-temperature steam application as well as for use with organic coolants. In addition, if we can cause the hydrogen that a pressure tube picks up to migrate to a region where it will not harmfully affect the structural integrity, then we can expect to increase the life of the tube. The finned pressure tube is such an approach, which we will be testing in-reactor in 1967.

4. FUEL

UO_2 FUEL (10)

The first fuel charge for the WR-1 reactor is pressed and sintered UO_2, enriched to 2.4 wt. % U^{235} in U and clad in Zr-2.5 wt. % Nb alloy. Some details are given in Tables III and IV. As an alternative we have had fabricated a half-charge of UO_2 clad in the SAP 895 alloy, (see also Tables III and IV). At present the main part of the fuel charge under irradiation is Zr-2.5 Nb clad. As a preliminary test, one site has been loaded with SAP clad UO_2 fuel.

Prototype elements of this fuel (both SAP and Zr-Nb clad) are just completing a long term irradiation in the X-7 loop in NRX in HB-40 coolant. A burn-up of 6000 MWd/Tonne U has been successfully achieved. The target burn-up is 8000 MWd/Tonne U. This, together with previous experiments in X-7 and U-3, gives us confidence that we will be able to meet the burn-up target in WR-1 without difficulty.

The only unusual occurrence to date has been the removal of one fuel string because of a suspected defect in the Zr-2.5 Nb cladding.

TABLE III

WR-1 FUEL GEOMETRY

	UO_2		UC	
	Zr-Nb Clad	SAP Clad	Zr-Nb Clad	SAP Clad
Enrichment wt. % U^{235} in U	2.4	2.4	2.7	2.7
Nominal bundle length (cm)	49.5	81.3	49.5	81.3
Bundles per channel	5	3	5	3
Elements per bundle	18	18	18	18
Clad. O.D.(mm)	15.1	15.4	15.1	15.4
Clad. thickness (mm)	0.635	0.635	0.635	0.635
Diam. clearance fuel to clad. (cold) (mm)	0.05-0.13	0.08-0.15	0.09	0.14

TABLE IV

WR-1 FUEL DESIGN PARAMETERS

(Maximum conditions)

	UO_2		UC	
	Zr-Nb Clad	SAP Clad	Zr-Nb Clad	SAP Clad
Element heat rating $Q/4\pi$ W/cm	40	40	44	44
Surface heat flux W/cm^2	105	105	115	115
Clad. surface temp. at 350^0C coolant outlet ^0C	435^0C	435^0C	427^0C	427^0C
Fuel center ^0C	∿2000	∿2000	795	1020
Target burn-up MWd/Tonne U	7500	7500	16000	16000

UC FUEL (13)

We now have one Zr-Nb clad UC fuel string under irradiation. A SAP clad UC string will be added shortly (Tables III and IV).

Previously prototype elements of SAP clad UC had been irradiated in the X-7 loop to a maximum burn-up of 11,100 MWd/Tonne U, at which time a cladding failure occurred. However, the UC in this irradiation was slightly hypostoichiometric (<4.8 wt. % C) which is somewhat more susceptible to irradiation swelling than is the hyperstoichiometric UC (4.8 - 5.0 wt. % C) which is being used in the WR-1 irradiation. The fuel was also operating at rather higher ratings than will be found in WR-1. An irradiation of SAP clad and Zr-2.5 Nb clad UC bundles was also performed in the U-3 loop in NRU to 2800 MWd/Tonne U. This had to be removed at that stage to make way for another experiment. However with our present knowledge we are reasonably confident that the design target of 16,000 MWd/Tonne U can be met with either cladding.

REFERENCES

(1) R.J. Graham, K.J. Gray, "WR-1 Design and Construction". Paper presented at 1966 CNA Conference, Winnipeg, Manitoba, May 31, 1966.

(2) A.J. Summach, "WR-1 Commissioning, Start-up and Operation". Paper presented at 1966 CNA Conference, Winnipeg, Manitoba, May 31, 1966.

(3) Canadian Nuclear Technology. Vol. 4, No. 4, p. 28 - 41, Fall 1965.

(4) R.F.S. Robertson, "Status Report on the WR-1 Reactor and Plans for Its Use in the AECL Research and Development Program". AECL report 2082. (September 1964).

(5) R.F.S. Robertson, "The Whiteshell Nuclear Research Establishment". To be published in: Chemistry in Canada.

(6) M. Tomlinson, M.G. Bailey, R.R. Tymko, "The Radiation Decomposition Characteristics and Physical Properties of Three Low Melting Organic Coolants for Reactors". AECL report 1915, November 1963.

(7) M. Tomlinson, J.L. Smee, E.B. Winters, M.C. Arneson, "Reactor Organic Coolants: 1. Characteristics of Irradiated Hydrogenated Terphenyls". To be published in: Nuclear Science and Engineering.

(8) M.C. Arneson, J.L. Smee, M. Tomlinson, E.B. Winters, "Some Characteristics of Irradiated HB-40: An Organic Liquid Coolant for Reactors". Paper accepted for presentation to the American Nuclear Society, Denver, Colorado, June 20-23, 1966.

(9) B.A. Finlay, J.L. Smee and S.R. Hatcher. "Organic Coolant Performance in Reactor Loops". Paper accepted for presentation to the American Nuclear Society, Denver, Colorado, June 20-23, 1966.

(10) R.G. Hart, I.E. Oldaker, H.E. Thexton, J.F. Walker, "UO_2 Fuels in Organic-Cooled Reactors". Paper accepted for presentation to the American Nuclear Society, Denver, Colorado, June 20-23, 1966.

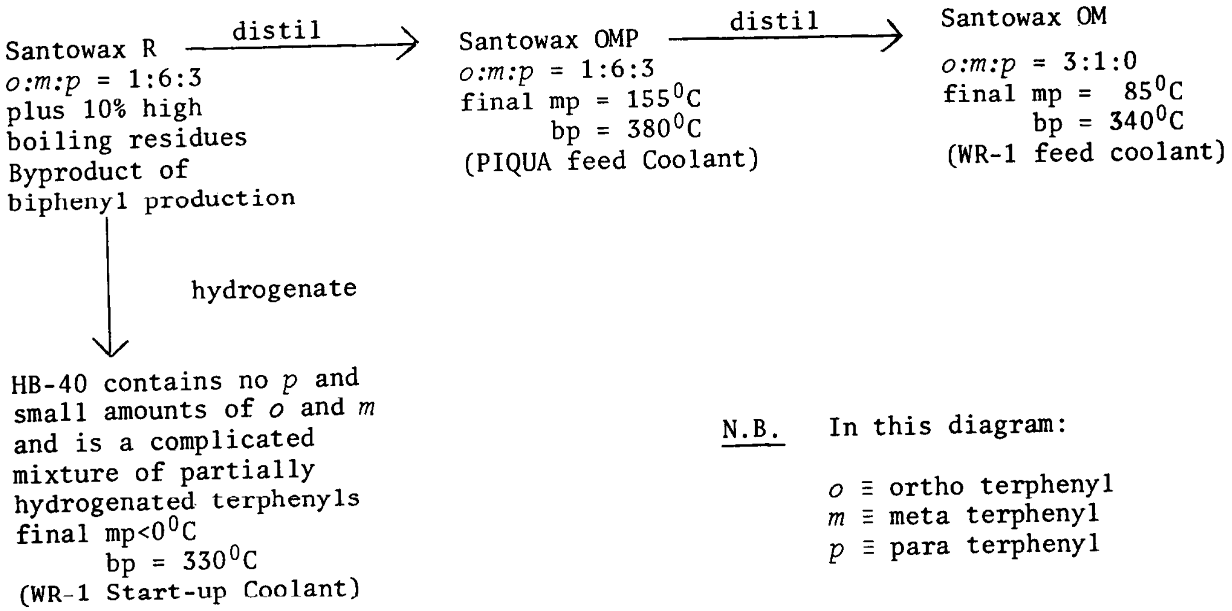
(11) J. Boulton, S.R. Hatcher, R.E. Hollies, "The Use of Zirconium Alloys in Organic Coolants". Paper accepted for presentation to the American Nuclear Society, Denver, Colorado, June 20 - 23, 1966.

(12) H.E. Thexton, B.J.S. Wilkins, A.C. Trupp, A. Sawatzky, "Prospects for Zirconium Alloy Coolant Tubes in Organic-Cooled Reactors". Paper accepted for presentation to the American Nuclear Society, Denver, Colorado, June 20 - 23, 1966.

(13) W.G. Mathers, R.D. MacDonald, J.E. May, A.M. Tachis, "UC Fuels in Organic-Cooled Reactor". Paper accepted for presentation to the American Nuclear Society, Denver, Colorado, June 20-23, 1966.

FIGURE 1

INTER-RELATIONSHIP OF SANTOWAX OM AND HB-40



N.B. In this diagram:

o ≡ ortho terphenyl
m ≡ meta terphenyl
p ≡ para terphenyl

FIGURE 2. HYDRIDING OF ZIRCONIUM ALLOYS IN ORGANIC COOLANT