REFERENCES

1. B.-G. BRODDA and D. HEINEN, "Solvent Performance in THTR Nuclear Fuel Reprocessing. Part II. On the Formation of Dibutyl Phosphoric Acid by Radiolytic and Hydrolytic Degradation of the TBP-*n*-Paraffin Extractant," *Nucl. Technol.*, **34**, 438 (1977).

2. C. V. SONNTAG, G. ANSORGE, A. SUGIMORE, T. OMORI, G. KOLTZENBERT, and D. SCHULTE-FROHLINDE, "Radiation Chemistry of DNA Model Compounds. Part II. Alkyl Phosphate Cleavage of Aliphatic Phosphates Induced by Hydrated Electrons and by OH Radicals," *Z. Naturforsch.*, **276**, 471 (1972).

3. Z. NOWAK and M. NOWAK, *Radiochem. Radioanal. Lett.*, **14**, *3*, 161 (1973).

4. A. S. SOLOVKIN, P. G. KRUITIKOV, and G. N. YAKOVLEV, *Russ. J. Inorg. Chem.*, **16**, *5*, 763 (1971).

5. G. KOCH, W. OCHSENFELD, H. SCHNIEDER, and W. WEINLÄNDER, *Kerntechnik*, **18**, 253 (1976).

REPLY TO "COMMENTS ON 'SOLVENT PERFORMANCE IN THTR NUCLEAR FUEL REPROCESSING. PART II: ON THE FORMATION OF DIBUTYL PHOSPHORIC ACID BY RADIOLYTIC AND HYDROLYTIC DEGRADATION OF THE TBP-*n*-PARAFFIN EXTRACTANT' "

It was clearly stated in the referred paper,[1] and the authors were well aware of the fact, that the parameters influencing the HDBP yield in TBP degradation are numerous. The authors very consciously limited their investigations to the application of a few parameters only, in order to get some basic but significant information on TBP behavior, recognizing the fact that actual process conditions were not fully simulated and again stating that not all questions are answered.

Saunders[2] is not correct in saying that the authors have considered only two of four degradation contributing reactions:

1. Hydrolysis of TBP in the aqueous phase was investigated by immediate extraction of HDBP into the organic phase during contact with nitric acid. The results are plotted in Fig. 4 of Ref. 1.

2. Radiolysis in the aqueous phase is implicitly included in the radiolysis experiments with a nitric-acid-equilibrated, which also means water-saturated, solvent. The result of this experiment was the reduction of the overall HDBP yield below the corresponding value from nitric acid/water-free solvent beyond a certain dose rate at a given nitric acid concentration in the organic phase. This is documented in Tables III and IV and in Fig. 6 of Ref. 1.

Moreover, Sonntag et al.[3] have not worked on TBP, but on trimethyl-phosphate in alkaline solutions, finding increasing G(acid) values with increasing pH. Their results may or may not be applicable to the Thorex extractant system, but they are certainly no proof for Saunders' criticism.

The presence of metal ions will indeed influence the behavior of the organic solvent. This, however, was not the purpose of this publication, but it may be the subject of a future work.

B.-G. Brodda

Kernforschungsanlage Jülich GmbH
Institute für Chemische Technologie
D-517 Jülich, Postfach 1913
Federal Republic of Germany

December 8, 1977

REFERENCES

1. B.-G. BRODDA and D. HEINEN, "Solvent Performance in THTR Nuclear Fuel Reprocessing. Part II: On the Formation of Dibutyl Phosphoric Acid by Radiolytic and Hydrolytic Degradation of the TBP-*n*-Paraffin Extractant," *Nucl. Technol.*, **34**, 428 (1977).

2. BARBARA B. SAUNDERS, "Comments on 'Solvent Performance in THTR Nuclear Fuel Reprocessing. Part II: On the Formation of Dibutyl Phosphoric Acid by Radiolytic and Hydrolytic Degradation of the TBP-*n*-Paraffin Extractant," *Nucl. Technol.*, **38**, 441 (1978).

3. C. V. SONNTAG, G. ANSORGE, A. SUGIMORE, T. OMORI, G. KOLTZENBERT, and D. SCHULTE-FROHLINDE, "Radiation Chemistry of DNA Model Compounds. Part II. Alkyl Phosphate Cleavage of Aliphatic Phosphates Induced by Hydrated Electrons and by OH Radicals," *Z. Naturforsch.*, **276**, 471 (1972).

COMMENTS ON "A GENERALIZED PARAMETRIC MODEL FOR TRANSIENT GAS RELEASE AND SWELLING IN OXIDE FUELS"

It is interesting that some of the predictions by Gruber[1] are diametrically opposite to the observed behavior of oxide fuels. Gruber's Fig. 15 predicts that gas release from oxide fuels will increase as increasing hydrostatic pressure or stress is applied.

It has been observed experimentally that when a stress is applied to cause the collapse of one of two samples containing lenticular voids, the voids remain in the unstressed sample and disappear in the stressed sample. These results have not been published, but the same phenomenon on a macroscopic scale is to be seen in Fig. 16 of Bain's report.[2] Bain's figure shows several drill holes, one of which has been reduced in diameter by thermal expansion stresses in the plastic central region of the oxide.

Since it is generally agreed that the migration of bubbles in the columnar grain region of oxide fuels is necessary for producing large amounts of gas release, it follows that if a stress is applied to reduce the size of or to eliminate these bubbles, then gas release will be diminished. This is not the result predicted by Gruber.

A possible explanation for this failure of Gruber's model may be found in the assumption that the bubbles in the columnar grain region are moving by a surface diffusion mechanism. It should be obvious that a bubble whose cross section looks like a plano-convex "lenticular" void is not responding to surface tension forces as a first-order determinant of its shape.

A physical explanation for the development of the "lenticular" shape of bubbles in oxide fuels was published by Oldfield and Markworth.[3] Their explanation is based on the migration of voids by sublimation of impure matter from the hot side of a void and condensation of purified matter as a crystal facet on the cold side of a void. Gas and other impurities are released to the void in the process.

Gruber's Figs. 15 and 16 suggest that swelling and gas release in oxide fuels are inversely related. This is contrary to principles proposed on the basis of experimental observations by Hilbert et al.[4] Their experiments show that swelling and gas release are sequentially coupled in oxide fuels at high temperatures. Swelling, and the accompanying bubble formation, is a necessary predecessor of bubble interlinkage, bubble migration, and gas release. See also, Iwano and Oi.[5]

Walston Chubb

3450 MacArthur Drive
Murrysville, Pennsylvania 15668

November 14, 1977

REFERENCES

1. E. E. GRUBER, "A Generalized Parametric Model for Transient Gas Release and Swelling in Oxide Fuels," *Nucl. Technol.*, **35**, 615 (1977).

2. A. S. BAIN, "Cracking and Bulk Movement in Uranium Oxide Fuel Elements," AECL-1827, Atomic Energy of Canada Limited (Sep. 1963).

3. OLDFIELD and MARKWORTH, *Mater. Sci. Eng.*, **4**, 353 (1969).

4. HILBERT, CHUBB, STORHOK, and KELLER, *J. Nucl. Mater.*, 38, 26 (1971) and *J. Nucl. Mater.*, **44**, 136 (1972).

5. IWANO and OI, *J. Nucl. Sci. Technol.*, **12**, 763 (1975).

REPLY TO "COMMENTS ON 'A GENERALIZED PARAMETRIC MODEL FOR TRANSIENT GAS RELEASE AND SWELLING IN OXIDE FUELS' "

I regret that my paper[1] apparently did not sufficiently identify the problems treated. I find no fault with the comments made by Chubb,[2] except that the points made in his letter do not apply to the paper in question.

The paper discusses transient fission gas release from unrestructured (or perhaps equiaxed) fuel grains to the grain boundaries. Release from the fuel pellet to its surroundings, or release to the central void, are not considered explicitly, nor is steady-state release.

Our approach has been that, at the onset of a rapid thermal transient typical of hypothetical conditions for a liquid-metal fast breeder reactor, most of the fission gas inventory will be associated with the cooler, unrestructured fuel. It is the release of this gas from the fuel, or fuel swelling caused by this gas, that can influence the course of a reactor accident by inducing reactivity feedbacks through fuel disruption or displacements.

Since transient gas release from unrestructured fuel does not depend on sweeping by lenticular voids, and since the columnar fuel is assumed to contain a negligible amount of fission gas at the onset of the transient, collapse of lenticular voids under pressure has no bearing on the problem treated in the paper.

Again, the point made in the paper concerning the inverse relationship between gas release and swelling refers to intragranular gas behavior: If gas is released from the grain, it cannot contribute to intragranular swelling. It can, however, contribute significantly to intergranular swelling, which is often the major component of fuel swelling. Intergranular swelling and release of gas from the fuel pellet through interlinked porosity are indeed sequentially coupled. In fact, a prior step in the sequence is the release of gas from the grain to the grain boundary. This step is the one assumed to be rate controlling and treated in the paper. The generalized parametric model can then be applied to define the source term for subsequent analysis of intergranular gas behavior, in much the same manner as an earlier and much less sophisticated model was applied by Hofmann and Meek.[3]

I appreciate this opportunity to clarify the realm of applicability and the purpose of my calculations.

E. E. Gruber

Argonne National Laboratory
Reactor Analysis and Safety Division
9700 South Cass Avenue
Argonne, Illinois 60439

November 29, 1977

REFERENCES

1. E. E. GRUBER, "A Generalized Parametric Model for Transient Gas Release and Swelling in Oxide Fuels," *Nucl. Technol.*, **35**, 615 (1977).

2. WALSTON CHUBB, "Comments on 'A Generalized Parametric Model for Transient Gas Release and Swelling in Oxide Fuels,'" *Nucl. Technol.*, **38**, 442 (1978).

3. J. R. HOFMANN and C. C. MEEK, "Internal Pressurization in Solid Mixed-Oxide Fuel Due to Transient Fission Gas Release," *Nucl. Sci. Eng.*, **64**, 713 (1977).