LETTERS TO THE EDITOR

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"

The application of conclusions based on laboratory experiments to process conditions is often difficult and should be done carefully, delineating the differences between the two conditions. Brodda and Heinen[1] point out that many experimental results appearing in the literature are not applicable to process conditions because insufficient attention is paid to the various contributions of experimental parameters that may not be the same under both laboratory and process conditions. Unfortunately, the authors' experimental results are similarly not directly applicable. Two major points are identifiable below:

1. Their experiments do not correctly resolve all contributions to tri-*n*-butyl phosphate (TBP) degradation.
2. Their experiments did not include consideration of the presence of metal ions.

The authors correctly state that dibutyl phosphoric acid (HDBP) is produced via two separate processes, the radiolytic and acid hydrolytic decomposition of TBP and that the literature does not correctly resolve the amount of HDBP formed into its radiolytically and hydrolytically produced fractions. However, the authors have likewise failed in that they did not further resolve the separately identifiable contributions from radiolysis and hydrolysis.

The amount of HDBP produced under process conditions is a sum of four reactions:

1. that due to direct radiolysis of TBP in the organic phase
2. that due to the radiolysis in the aqueous phase, where the reaction of the OH radical with TBP produces HDBP (Ref. 2)
3. that due to the hydrolysis of the TBP which occurs in the organic phase as a result of the acid extracted into it
4. that due to the hydrolysis of the TBP in the aqueous phase.

Brodda and Heinen have considered only two of the above reactions, the radiolysis and hydrolysis reactions of TBP occurring in the organic phase after a prior contact with nitric acid. Under actual process conditions, the major radiation occurs during the intimate mixing of the organic phase and the aqueous feed. Thus, the amount of HDBP produced by Brodda and Heinen in these experiments is only a lower limit of that expected to be formed under process conditions. Their conclusion that, under the Thorex process considered, the radiation damage is small, since 85% of the HDBP is formed via acid hydrolysis, is not valid.

The presence of metal ions, especially Th(IV), Pu(IV), and Zr(IV), strongly influences the behavior of the organic solvent. There have been reports indicating that the presence of Zr(IV) has a synergistic increase in the amount of TBP decomposed by radiolysis.[3] Thus, under process conditions, the metal ions may be responsible for a greater extent of decomposition than occurs during laboratory experiments that do not include these metals. Regardless of the source of HDBP, once it is formed, Zr(IV), Th(IV), and Pu(IV) will form dibutyl phosphate complexes that cannot be removed from the organic phase with a simple caustic scrub.[3-5] In fact, as Brodda and Heinen point out, the alkaline washing can increase the amount of HDBP by adding alkaline hydrolysis to the list of reactions decomposing the TBP. If, for example, TBP-complexed Zr(IV) or Th(IV) is in the organic phase during the wash, they may be converted to the less easily scrubbed dibutyl phosphate complexes.

It is especially inappropriate for authors criticizing the application of laboratory data to process conditions to make the same mistake themselves. To dismiss problems in a process on the basis of experiments that do not include some of the major sources of the problems without carefully qualifying the conclusions is irresponsible.

As a final note, this paper was confusing, poorly written, poorly edited, and poorly referred. Technical points such as the time dependence of the yield of HDBP formed by hydrolysis were mentioned, but no data were included to show the nature of the dependence. The authors mention the unexpected result that they did not observe any H_2MBP in direct contradiction with previous literature, but nowhere was there any explanation of why this might have occurred. In the interests of maintaining the high quality of the Journal, more careful attention should be paid to the refereeing of papers.

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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).

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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.

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REFERENCES

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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