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OAK RIDGE NATIONAL LABORATORY

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TO: F. L. Culler

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For The Atomic Energy Commission

Chief, Declassification Branch TC

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SUMMARY

Homogeneous Reactor Chemical Processing

Tc^{+7} is soluble to the extent of at least 9.7 g/kg H_2O in reactor fuel solution at 250°C . Tc^{+4} is soluble only to about 10-20 mg/kg H_2O in uranyl sulfate solutions at 284°C . Under conditions where Tc^{+7} was reduced to Tc^{+4} uranium was also reduced and precipitated from solution.

Volatility Studies

Residual uranium contents of 18-26 weight % were obtained in further work on the decomposition of $3 \text{ NaF} \cdot \text{UF}_6$ complex at elevated temperatures in a closed system. The presence of excess F_2 reduced the residual uranium content to 14%. Analyses of the product by an oxidation procedure indicated that the residual uranium was in the pentavalent state.

Fused Salt Processing

A black solid containing uranium metal and oxides of zirconium and uranium was formed on dissolution of STR fuel in a fused fluoride salt with HF.

Feed Materials

The retorting of surface amalgamated Zircaloy-2 specimens which were coated with titanium amalgam at 450°C did not produce an adherent titanium coating. Retorting at 1025°C produced some Ti coating which could be removed by hard scraping.

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1.0 HOMOGENEOUS REACTOR CHEMICAL PROCESSING

(R. A. McNees)

1.1 Fission Product Chemistry (R. A. McNees)

In the presence of hydrogen gas (50 psi at room temperature) Tc^{+7} , as $KTcO_4$, in uranyl sulfate solution at $284^\circ C$ in quartz tubes was reduced to a lower valence state and precipitated from solution. Most of the uranium, originally present at 5 g U/kg H_2O , also precipitated. The final concentration of Tc was 12 mg/kg H_2O compared to an original concentration of 1000 mg/kg H_2O . Under the same conditions no change in solutions containing 1 g rhenium per kg H_2O as $KReO_4$ was observed.

In small quartz tubes which could be observed while being heated TcO_2 did not dissolve to any appreciable extent in 5 g U/kg H_2O solutions when only air was present in the vapor phase, but it did dissolve readily at $250^\circ C$ when O_2 was present. In one experiment a solution of 9.7 g of Tc/kg H_2O was obtained with no evidence that this is an upper limit.

From the foregoing observations it can be predicted that Tc will be soluble in reactor soup if the +7 state is stable, but will not be soluble above 10-20 mg/kg if Tc^{+4} is the stable valence state under reactor conditions.

2.0 VOLATILITY STUDIES

(G. I. Cathers)

2.1 UF₆ Complex Studies (R. L. Jolley)

Further data on the decomposition of 3 NaF·UF₆ at elevated temperatures in a closed system was obtained in five runs. The primary objective in the work was the development of a more suitable apparatus and procedure for studying the effect. In four runs conducted at $400^\circ C$ for 1-4 hours the residual uranium content varied over the range of 18-26%, in agreement with

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previous work. When excess F_2 was used, the uranium content was reduced to 14%. A value of 20% residual uranium was calculated to correspond to approximately 31% decomposition of the originally sorbed UF_6 . No significant correlation was apparent in this scouting work as to the effect on the extent of decomposition of the initial UF_6 pressure, or length of time that the material was kept at $400^\circ C$.

The residual uranium present in the product of all runs was pentavalent based on analytical results. The tetravalent uranium content in each case was approximately equal to the hexavalent content as a result of disproportionation of pentavalent state in the analytical procedure. The analytical method being used at present involves measurement of the U^{+4} by an oxidation-reduction procedure, followed by determining the total U content colorimetrically. Use of either this procedure, or of the leaching procedure previously described, appears equally applicable in determining the U^{+4} and U^{+6} content. An attempt was made to determine gravimetrically the amount of F_2 evolved in each run by sorbing the F_2 in a NaCl trap. However, a significant amount was detected only in the fourth run where 23% of the theoretical quantity was found.

3.0 FUSED SALT PROCESSING (R. G. Wymer)

When a piece of STR element is dissolved in fused fluorides using HF gas, a black substance forms on the surface of the piece, and pieces of it pervade the melt. A melt was broken up and the black pieces were sorted out and x-ray analyzed. The black material contained the following substances:

U Metal,

$ZrOF_2$

UO_2

ZrO_2

UF_4

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Surprisingly, the following substances were not found:

NaF,

ZrF₄

Zr (α phase),

U₃O₈

There were also lines for a metastable compound whose composition lay between NaZrF₅ and ZrF₄. (This compound has been formed by other workers by adding sodium to ZrF₄ and quenching the melt from above 600°C, and has been observed to disappear upon standing in air). Nickel fluoride may also have been present, but overlapping lines made a positive identification very difficult.

4.0 FEED MATERIALS (O. C. Dean)

4.1 Metallex (C. P. Johnston)

4.1.1 Coating of Zircaloy-2 by Metallex Techniques

Two samples of Zircaloy-2 were amalgamated at the surface by cleaning in a molten ZnCl₂-KCl-NaCl bath at 450°C, zinc-dipping at 450°C and finally boiling in mercury for 72 hours to remove the zinc and replace it with mercury. A concentrated (~2%) titanium quasi-amalgam was applied in a heavy layer to the amalgamated samples. One sample was retorted in a stream of argon at 450°C to remove mercury and the other at 1025°C. The sample retorted at the lower temperature had a flaky, oxidized surface on all sides, with no evidence of adhering titanium residue. The sample retorted at the higher temperature had a flaky, oxidized surface on top where it contacted the argon, but on the under side, which was close to the supporting tantalum square, some adherent titanium metal was observed. This metal could be removed by scraping, and was not as tightly-adherent as that produced in previous experiments where the coating of zinc had not been removed before application of the titanium quasi-amalgam.

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The flaky, oxidized surfaces and adherent metal coats on the under sides of the retorted samples suggested that the furnace atmosphere or the amalgam were not oxygen-free, and that this may have been the reason for non-adherence of titanium to the Zircaloy-2 in the previous experiments.

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