ITER TASK T299 (1996):  
FUEL CLEANUP SYSTEM DEMONSTRATION TESTS

CFFTP G-9722
May, 1997

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CFFTP GENERAL

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1. TASK OBJECTIVES

The objective of this task is to demonstrate processes for efficient cleanup and detritiation of the plasma exhaust. In this subtask, the objectives were to provide further design data on the HITEX process, and to build and demonstrate 2-stage high-detritiation HITEX performance.

2. BACKGROUND

The original concept proposed for detritiating impurities in the ITER plasma exhaust was based on a batch HITEX process that uses catalyst-assisted isotopic exchange of tritium bound to impurities with protium and extraction of the resulting elemental tritium with a permeator [1, 2]. The main advantage of this process is that it is simple, does not produce tritiated water and is capable of achieving high detritiation factors (DFs).

Following successful proof-of-principle tests at Ontario Hydro [3], preliminary tritium tests were carried out at Chalk River Laboratories (CRL) with tritiated methane (CQ, Q = H, D or T) and mixed CQ/He mixtures under ITER Task T49 in 1994 [4, 5].

In the batch-HITEX process, impurity detritiation is characterized by an initial fast-detritiation step followed by a slow-detritiation step. The slow-detritiation step, which is detrimental to the overall detritiation process, is the slow desorption of tritium from contaminated surfaces. Under the conditions tested in 1994, ~99.99-99.999% of the initial activity was removed in the fast-detritiation step corresponding to a Detritiation Factor (DF) in the range 1x10^4-1x10^5. At higher DFs (>1x10^5), the detritiation rate slows down consistent with a slow surface-outgassing process.

A simple model was developed to describe the HITEX process based on the following simplifying assumptions:
1. complete mixing of gases,
2. complete isotopic equilibrium of hydrogen isotopes among gases at the outlet of the reactor, and
3. constant, isotope-independent hydrogen isotopes recovery fraction of the permeator.

From a simple mass balance for tritium in the tank, the DF can be shown to be given by:

\[ \text{DF} = e^{\lambda t} \]  
\[ \lambda = \frac{Q_L}{V_{imp}(1+R)} \left[ f_{Q2} + R \left( \frac{f_{Q2eq}}{f_{Q2eq}} + R \right) \right] \]

where:
- \( Q_L \) is the loop recirculation flow rate at the operating conditions (L/min),
- \( R \) is the molar ratio \( V_{H2}/V_{imp} \) (where \( V_{H2} \) is the tritium-free hydrogen added to the tank initially and \( V_{imp} \) is the number of impurity moles in the tank),
- \( f_{perm} \) is the isotope-independent hydrogen isotopes recovery fraction of the permeator,
- \( f_{Q2} \) is the mole fraction of \( Q_2 \) gas present initially in the impurities \( V_{imp} \), and
- \( f_{Q2eq} \) is the mole fraction of equivalent \( Q_2 \) in \( V_{imp} \).

According to the model, under complete isotopic equilibration in the reactor and perfect mixing conditions, the DF is a simple exponential function of time with the pre-exponential factor determining the detritiation rate. The model was shown to be consistent with the fast-detritiation step and agreed well with the observations: DF increased with \( Q_L \), DF increased with \( R \), and no initial tritium concentration effects. The model was found to agree well with the experimental...
data at high recirculation flow rates (5 L/min (STP) while underpredicting at lower flow rates (2 L/min (STP)). This was attributed to poor mixing conditions in the tank (perfect plug flow conditions would keep the reactor feed at the highest possible tritium concentration) that would increase the average detritiation rate.

Further tests in 1995 explored the effects of variable feed compositions, catalysts and flow rates [6]. Notably, experiments were carried out under humid gas conditions up to ~50% relative humidity. At the outlet of the permeator, the gas is enriched with impurities and can lead to water vapor condensation. To avoid water vapor condensation at the outlet of the permeator, these areas were heat traced to 80-100°C. Also, three catalysts were tested, with an AECL platinum/silicalite catalyst on a wire mesh support found to be best, probably due to the low moisture retention in silicalite. In these 1995 tests, with the improved catalyst and trace-heated system, we found that DFs ~ 10^4 could be achieved quickly under wet or dry conditions (Figures 1 and 2).

Also in 1995, we carried out first tests with a 2-stage HITEX loop in which the first stage was a once-through HITEX and the second-stage was a batch HITEX, in order to improve the overall process DF. In the experiments, the measured first stage DF was ~7-8, consistent with theoretical estimates for the particular feed conditions.

Furthermore, in 1995 we undertook first HITEX-like tests in the FzK Tritium Laboratories CAPRICE loop at high tritium concentrations (up to 90 kCi/m^3). In these tests, the large Ni cracking catalyst was used as the HITEX isotope exchange catalyst. However, in these limited tests, the DF was < 100. This low DF was attributed to large moisture retention in the Ni catalyst, as well as other limitations in the loop which was not originally designed for HITEX operation.

In 1996, we undertook to rebuild our FCU component test loop in order to correct some known deficiencies in the loop design, and to test alternative first-stage processes such as the CAPRICE and PMR1 concept, with a batch-HITEX final “polishing” stage. In particular, the 2-stage HITEX loop had developed over time and was not optimized - for example, it was crowded, had several dead-ended pipes and was not trace-heatable everywhere. These loop changes were substantial, and occupied almost all of our effort in 1996 - the loop changes are described here, but there were no experimental results.

Also in 1996, in collaboration with FzK, we undertook PERMCAT tests in a special loop at AECL and further HITEX tests at the CAPRICE loop with a specially-build HITEX catalyst and appropriate loop modifications.

3. LOOP UPGRADE AT AECL CRL

3.1 Experimental Setup

The experimental facility is located in the Tritium Laboratory at CRL. A schematic diagram of the 2-stage FCU loop is given in Figure 3. The entire loop is designed to operate at up to 80°C to minimize tritiated moisture holdup in the system. This required use of specialized pressure, temperature and mass-flow gauges. Also, the loop was transferred to a larger glove box to allow greater room for the process equipment, and the glovebox ventilation system was upgraded. A flexible labmanager software control was setup to allow various modes of operation.
3.2 First Stage

The first stage was a permeator-reactor - basically a standard hydrogen permeator modified so that it could operate in a variety of modes, including once-through HITEX, CAPRICE, PERMCAT and PMR (Figure 4). Conceptually, the main change was to add catalyst to the shell side of the permeator. In all operating modes, the impurities are fed across the shell (catalyst) side of the permeator-reactor and detritiated impurities extracted on the far side. In once-through HITEX mode, H\textsubscript{2} is also added to the impurity feed and isotope exchange occurs in the catalyst, with the tube side blanked off. In CAPRICE mode, the impurities are simply allowed to crack as they flow across and out the far side, with the tube side blanked off. In PERMCAT mode, a counterflow of H\textsubscript{2} is fed through the tube-side to exchange the tritium in the impurities with the tritium-free H\textsubscript{2}. In PMR mode, tube side is actively pumped to low pressure to withdraw Q\textsubscript{2} from the impurities in order to crack the Q\textsubscript{2}O and CQ\textsubscript{4}. In each mode, different catalyst temperatures would be appropriate, as per the literature. And other combination modes can also be considered. Of course, the trade-off in this flexibility is that the performance may not be fully optimized for any given mode of operation, but this is acceptable for the present experimental focus on exploring the various detritiation modes that have been proposed for ITER, and for testing a different operating point than is under test by the other Home Teams.

The actual reactor design is a modified RSD Model 50 permeator. The main changes needed were to add catalyst to the shell side of the permeator. Dimensions were also adjusted slightly. The reactor was designed to operate at over 500°C (as needed for PMR mode), and contains about 4 L of catalyst. The final outer dimensions were 11” diameter and 28” between the sealing surfaces. All electrical and thermocouple connections were made at the flanged end of the unit. This reactor had the following parameters: catalyst volume ~4 L catalyst volume (~4 kg catalyst mass), 608 cm\textsuperscript{2} Pd surface area, and 5 Pd capillaries of 4’ length. For comparison, the LANL PMR1 unit tested in 1995 (by LANL) had 6.8 L catalyst volume and 380 cm\textsuperscript{2} Pd surface area.

3.3 Second Stage

The second stage was a batch-HITEX stage, with a 15 L storage volume, recirculating pump, isotope-exchange catalyst, permeator, and feed gas and H\textsubscript{2} addition points. This loop was configured to run in a “fast HITEX” mode, in which the actual HITEX loop volume is small and therefore can be quickly detritiated. Modelling of the HITEX process indicates that the loop size has no direct effect on the net processing rate or on the required amount of hydrogen swamping, but does drive the tritium inventory. The loop was designed to operate at 80°C, with reasonable care taken to minimize dead volumes.

3.4 Results

The loop was fabricated in 1996, and commissioned in early 1997. Experimental results will be described in the 1997 ITER task report.
4.0 HITEX TESTS AT FZK

4.1 Experimental Apparatus

In order to carry out the second set of HITEX mode tests in the CAPRICE loop, the following changes were necessary:
- avoid catalyst beds with significant retention of carbon and/or water;
- minimize dead legs as much as possible;
- avoid water vapor condensation in the loop.

To achieve these objectives in 1996, the plan was to install a new specially-built HITEX reactor in the PERMCAT position in the secondary CAPRICE loop, to modify the loop to minimize dead volumes, and to incorporate HITEX-relevant instrumentation and control loops.

Figure 5 illustrates the dedicated HITEX reactor that was installed in the loop for HITEX mode operation. This reactor used two AECL Pt/silicalite catalyst modules to ensure good performance (our previous AECL tests under similar flow rates had used only one). It also incorporated features important for any "industrial" application - basically all access is from one end and the entire reactor is encased in a secondary pressure vessel (not shown in Figure 5). The component was fabricated by FzK.

Figure 6 illustrates the CAPRICE loop with HITEX mode operation. A 3.9 L buffer volume is kept in-line, giving a total loop volume of 6-7 L. Physically, the HITEX reactor was placed far to the left of the valves within the glovebox (close to the 10 L volume) because of space limitations, and was connected with approximately 10 m length of 1/4" tubing. The secondary CAPRICE loop was modified as much as practical to minimize dead legs, but it was not possible to completely eliminate them. After modifications we estimated that there were still about 18 significant dead volumes (5-10 cm3) in the loop, of which 9 are due to on-line instruments and four are due to bypass lines.

Additional control points added to the system, including 2 heaters and 5 thermocouples in the HITEX reactor, one new ion chamber at the inlet of the HITEX reactor (RXH01), a new D2 addition mass flow controller able to handle the desired flow range of 0-2 L/min, one new loop pressure transducer, and 2 new ion chambers installed in GC system. The D2 addition mass flow controller was controlled by the new loop pressure transducer (RP 139), installed upstream of the 3.9 L buffer volume.

4.2 Experimental Procedures

The high activity tritiated methane needed for the experiments was prepared in the primary-CAPRICE loop by isotopic exchange of CD4 with pure tritium. The loop configuration used to prepare tritiated methane was similar to the batch HITEX loop. Pure tritium stored in the 20 L buffer volume in the primary CAPRICE loop was mixed with CD4 that was continuously fed in to the loop and flowed through exchange reactor containing Ni/Kieselghur catalyst. The CD4 content in the reactor feed was kept small (<5%) to ensure near-complete conversion of CD4 to tritiated methane in the reactor. The equilibrated gas mixture was then passed through the permeator and the DT gas recovered was circulated back to the buffer vessel while tritiated methane was stored in the 10 L vessel in the secondary-CAPRICE loop.
A typical experimental run started by filling the HITEX loop (with the permeator by passed) with tritiated methane to the desired pressure. The loop was then filled with He and D₂ with appropriate amounts to a total loop pressure of ~950 mbar. After mixing the gases thoroughly, a gas sample was taken for analysis by gas chromatography (GC) to determine the gas composition and initial tritium activity. After adjusting the recirculating flow rate to the desired value, the experimental run was started by switching the recirculation flow through the permeator. The loop operation (pressure, temperature, humidity and flow rates) was monitored continuously with the online instruments. The detritiation performance was monitored both with on-line ionization chambers and by periodic (approximately every 10 min) off-line GC analysis of loop-gas samples. The length of an experimental run was limited to approximately 60 min. This run time was dictated by the DT-holding capacity of the isotope separation system.

4.3 Results

A series of 5 runs were made with the CAPRICE loop configured in the HITEX mode. The experimental conditions are listed in Table 1. The loop volume is estimated as 6 L (within 25%). The loop pressure was typically 950 mbar after the pump (RP 106), 930 mbar after the permeator (RP 124), and assumed to be around 900 mbar in-between these points. The typical glovebox temperature during the runs was 25°C. The impurity gas was essentially composed of tritiated methane and helium. However, the exact composition was not readily controlled. Low levels of hydrogen may have been present, along with water (-50 to -60°C dewpoint), and higher hydrocarbons.

The experiments were carried out at approximately similar impurity processing rates to our previous AECL tests. The key differences, however, were the use of higher tritium levels (0.1-0.5% T/H), lower swamping hydrogen ratios, D₂ swamping rather than H₂ swamping, and a different test loop. Based on our understanding of the HITEX process, we did not expect to find significant differences in the detritiation behavior as a result of high tritium levels or D₂ swamping. However, we expected possible effects from lower swamping and a different test loop that would help our understanding of the HITEX process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run #1</th>
<th>Run #2</th>
<th>Run #3</th>
<th>Run #4</th>
<th>Run #5</th>
</tr>
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<tbody>
<tr>
<td>Initial tritium activity, Ci/m³</td>
<td>51400</td>
<td>116200</td>
<td>64700</td>
<td>86200</td>
<td>217400</td>
</tr>
<tr>
<td>Ratio R = mol added D₂/mol impurity</td>
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<td>1.4</td>
<td>3.9</td>
<td>3.7</td>
<td>0.71</td>
</tr>
<tr>
<td>Ratio R² = mol tritiated organic/mol He in impurity</td>
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<td>1.3</td>
<td>2.4</td>
<td>6.8</td>
<td>0.75</td>
</tr>
<tr>
<td>Recirculation flow, mol/hr*</td>
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<td>2.7</td>
<td>2.9</td>
<td>3.0</td>
<td>7.1</td>
</tr>
<tr>
<td>D₂ addition flow, mol/hr</td>
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<td>1.5</td>
<td>2.4</td>
<td>2.4</td>
<td>2.9</td>
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<td>Loop pressure, mbar</td>
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<tr>
<td>Reactor temperature, K</td>
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<td>673</td>
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<td>673</td>
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<td>Permeator temperature, K</td>
<td>673</td>
<td>673</td>
<td>673</td>
<td>673</td>
<td>673</td>
</tr>
</tbody>
</table>

* Calculated from the D₂ addition flow rate assuming all D₂ is recovered on each pass through the permeator.
The experiments were limited in number and duration because of the accumulation of tritiated hydrogen that had to be processed by the isotope separation system, and because they were conducted during the short-term attachment of L. Rodrigo (AECL) to the FzK Tritium Laboratory.

The experimental results for these five runs are shown in Figures 7 to 11. The detrinitation factor was measured by both the on-line ion chamber and the GC ion chamber. The on-line ion chamber clearly showed background contamination, and approached a signal limit of around 6000-8000 pA from an initial signal of 200,000-800,000 pA (depending on the run). The GC tritium signal had a much lower background level (typically ~ 1 Ci/m3), so was able to measure DF better and is relied on in the following discussion. This GC DF signal shows the normal HITEX fast-detrinitation phase, followed in some runs by indications that a slower detrinitiation phase was approached. The results of applying the standard HITEX model to the CAPRICE loop conditions are also shown on the figures, and illustrate that in general the results are as expected (the permeator efficiency was assumed to be 99% due to the very large surface area available). Within these tests, DFs ~ 1000 were clearly achieved. However, in general, the tests were stopped at this point (due to limits on accumulated deuterium) and it was not possible to determine the “fast” DF turnover point in any case except Run #1.

Run #1 was notable in that a valve connecting a length of piping into the HITEX loop was accidentally left open. In addition to this long and thin dead volume, there are also a number of short deadlegs due mostly to valve T-off sections and to instrumentation legs. These dead volumes are not swept by the recirculating gas, so any initial impurities that fill these regions are only recovered on the time scale for the impurities to diffuse into the main loop. If this is longer than the loop cleanup time, then the diffusion time from these deadlegs will control the rate of detrinitiation. This can be modelled by simple gas exchange between the deadvolume gas and the loop volume on a diffusion time scale of \( L^2 / D \). The resulting equations must be integrated to determine the DF versus time.

In the CAPRICE loop, we estimate there were about 16 valve/instrumentation deadlegs on the loop, with 0.5" OD piping and 5-10 cm open lengths, for a total dead volume of around 130 cm\(^3\). In Run #1, the section of piping left connected was estimated to be 60-100 cm\(^3\) volume and around 30 cm length. The diffusivity were estimated as 4e-5 m\(^2\)/s, based on an approximate analytic model, specifically for the case of D\(_2\) diffusing in CD\(_4\) [8].

Solving the HITEX loop detrinitiation with gas exchange with these dead volumes results in the curve “Model-DV” shown in Figure 7 for Run #1 (specifically, 8 cm instrument deadlegs, 100 cm\(^3\) extra line deadvolume). The dead volume effect clearly is sufficient to explain the turnover in this case, within the experimental errors and the uncertainties in parameters (e.g., loop volume, dead volume).

In the other Runs #2-5, the dead-volume model was also applied using only the standard instrumentation deadlegs, as the valve had been closed for these runs. The diffusion time scale is much faster in these cases as the deadlegs were only few cm long, and did not have any significant effect in these cases. This is consistent with the reasonable fit between the standard HITEX model and the GC-measured DF (Figures 8-10).

Run #5 was the only case in which we did not obtain reasonable agreement between the standard simple HITEX model and the detrinitiation rate. This run was notable in that the amount of
swamping deuterium was deliberately made very low. It appears that the exchange was much slower than expected in the model (which assumes complete isotopic equilibration within the catalytic reactor) under these low-hydrogen cases. Therefore, we recommend operating away from very low swamping ratios (R < 1).

5. PERMCAT TEST AT AECL CRL

As followup to the PERMCAT tests conducted at AECL in 1995, a second series was conducted in 1996 - again in collaboration with FzK. In the 1996 tests, the experimental setup was modified for better measurement of the detritiation factor, and the PERMCAT component was modified to allow testing the effect of different capillary sizes and to obtain data at the midpoint of the PERMCAT column.

In the tests, 10-47 sccm (steady) of tritiated methane, hydrogen and helium (typically 0.25% CQ4/0.25% Q2 and balance He) were fed into the impurity side of the PERMCAT component, while 2-10 sccm of H2 were fed into the hydrogen inlet. The tritium content of the feed was around 12-15 kCi/m3. After catalytic exchange and permeation, the exiting impurity stream showed a detritiation factor of up to 700,000, depending on the feed conditions and the size of the internal capillary (which was varied from 1.6-2.36 mm OD). The results are described in detail in Ref.[7,9], and are not repeated here.

6. CONCLUSIONS

In 1996, the test program continued testing of the HITEX concept under different conditions (notably at high tritium levels, an independent test loop, and at low swamping ratios), and construction and commissioning of a 2-stage fuel cleanup system, and tritium testing of the PERMCAT concept.

With respect to the PERMCAT concept, very high detritiation factors were confirmed in the 1996 series of tests.

With respect to the HITEX process, the conclusions are as follows:
- HITEX performance continues to be in reasonable agreement with the standard model, except at very low hydrogen swamping ratios (R < 1) where performance is significantly reduced;
- DF > 10^3 were reliably achieved in the FzK CAPRICE loop modified for HITEX operation, using the Pt/silicalite catalyst; higher DFs may be achievable in longer runs with better control of dead volumes.
- “dead volumes” should be avoided in the HITEX loop; their effect can be estimated by simple changes to the standard HITEX model.

With respect to the 2-stage fuel cleanup system, a “generic” first stage plus a HITEX second stage loop was designed, built and commissioned in 1996. Testing of this loop is the main task for 1997.
REFERENCES


Figure 1. HITEK performance with the Pt/Silicalite catalyst showing consistent performance against previous Pt/Al2O3 catalyst even with humid feed.
Figure 2. Summary of HITEX performance with Pt/Silicalite catalyst, showing effects of composition and flow rate.
Figure 3. Upgraded AECL two-stage Fuel Cleanup Loop schematic.
Figure 4. Schematic of reactor-permeator component installed in the AECL loop.
Figure 5. Schematic of HITEX reactor component installed in FZK CAPRICE loop (secondary containment not shown).
Figure 6. Schematic of FzK CAPRICE loop as operated in HITEX-like mode.
Figure 7. HITEX Run#1 in FzK CAPRICE loop. The model results are based on the standard simple HITEX model ("Model"), and the simple HITEX model with the effect of dead volumes added ("Model-DV"). GC refers to point measurements with the GC system, while IC refers to the on-line ion chamber reading. Saturation of the on-line ion chamber is apparent at high background signals. The GC signal, with a lower background signal, shows a turnover due to a long dead volume related to a valve accidentally left open during this run.
Figure 8. HITEX Run#2 in FzK CAPRICE loop
Figure 9. HITEX Run#3 in FzK CAPRICE loop
Figure 10. HITEX Run#4 in FzK CAPRICE loop
Figure 11. HITEX Run#5 in FzK CAPRICE loop. This run had the lowest hydrogen swamping ratio (~0.7), and it appears that the exchange rate was much slower than predicted by the simple HITEX model under these conditions.