Contract No:

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Heat and Mass Transfer Study to Understand Thermal-Cycling Absorption Process (TCAP) Scale-Up Issues

The first-year goal of this study was to better understand the underlying physics affecting the separation capability of TCAP in order to provide a strong technical basis for design of a scaled up mega-TCAP, of interest for fusion and other potential applications.

Assessing mass transfer factors, researchers performed an extensive review and evaluation of prior theoretical work, mathematical models, and experiments on chromatographic separation. This effort resulted in the discovery of a previously unidentified factor impacting TCAP column scale-up. A model derived by J. Calvin Giddings indicates that the *combination* of coiling a packed column and increasing the column tube radius will decrease column separative performance.

This discovery prompted an in-depth review and reanalysis of data from SRNL TCAP column testing that had been performed in 2004. Comparison of the performance of straight versus coiled packed columns revealed that column coiling reduced separative performance by about a factor of 2.5. This reduction in separation capability is consistent with predictions from the Giddings model.

To assess heat transfer issues, SRNL researchers teamed with the Auburn University Center for Microfibrous Materials Manufacturing. Work by Auburn indicates that microfibrous entrapped sorbents (MFES) made from copper microfibers and palladium packing material could provide more uniform temperatures, faster heat transfer, and reduced cycle times in larger diameter TCAP columns.

Awards and Recognition

None to date.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

Signature **Date**

Heat and Mass Transfer Study to Understand Thermal-Cycling Absorption Process (TCAP) Scale-Up Issues

Project Team: Steve Xiao, Ben Randall, Bob Rabun, Boone Thompson, Bruce Tatarchuk

Subcontractor: Auburn University

Thrust Area: NS with application to ES and SEM

Project Start Date: October 1, 2018
Project End Date: September 30, 2019

TCAP was invented by SRNL and is a world-leading technology in hydrogen isotope separation, a critical process for fusion energy development and scientific research. External interests/inquiries have been received for as high as a 1000-fold throughput increase over the currently available TCAP system. This study determined a major factor impacting TCAP column scale-up. A model derived by J. Calvin Giddings indicates that the combination of a coiled packed column and an increase in the column tube radius results in reduction of column separative performance.

Reevaluation of data from SRNL TCAP column testing performed in 2004 indicates that the results are consistent with the Giddings model.
Work with the Auburn University Center for Microfibrous Materials Manufacturing indicates that microfibrous entrapped sorbents (MFES) made from copper microfibers and Pd/K could resolve issues with channeling and improve heat transfer and cycle time in TCAP columns.

FY2019 Objectives

Understand the fundamental physics of the efficiency losses previously noted during the 2004 HT-TCAP scale up and devise means to overcome them through the following:

- Determine the factors affecting and affected by TCAP gas mass transfer
- Determine the factors affecting and affected by TCAP heat transfer.

Introduction

TCAP is a palladium-based chromatographic process invented by Myung Lee in SRNL in 1980 and is a world-leading technology in hydrogen isotope separation.[1,2] Hydrogen isotope separation is a critical process for fusion energy development and scientific research. External interests/inquiries have been received for as high as a 1000-fold throughput increase over the current TCAP system.

Success with TCAP Scale-down

SRNL has been successful in *scaling down* the size of TCAP while maintaining the required capacity (Compact-TCAP, Mini-TCAP, Micro-TCAP).[3] Results from this study suggest that, among other improvements, some of the success of TCAP size-reduction efforts comes from reducing the tube diameter.

Figure 1: Successful Scale-down of TCAP systems

Issue with TCAP Scale-up

TCAP *scale-up* has been more difficult. In 2004 a newly-installed, scaled-up hydrogen-tritium TCAP system (HT-TCAP) demonstrated unexpectedly low separative performance.[4,5] SRNL performed extensive testing to explain and improve HT-TCAP performance. With the results of this testing, the flowsheet and operating parameters were optimized allowing the project to be completed successfully and on time. However, though the immediate project concerns were addressed, an unexplained and substantial gap remained between the expected separation and the actual HT-TCAP performance.

This project seeks to develop a clear understanding of the issues affecting TCAP scaling and enable the application of SRNL TCAP technology to the need for very-large-scale hydrogen isotope separation in fusion energy research, other nuclear applications, and environmental protection.

Approach

- Performed an extensive review and evaluation of prior theoretical work, mathematical models, and experiments on chromatographic separation including palladium chromatography.[6,7,8,9]
- Reviewed and re-evaluated data and results from the 2004 tests in support of the HT-TCAP project.
- Worked with Auburn University to evaluate microfiber-entrapped sorbents for application to TCAP to improve heat transfer and potentially improve mass transfer.

Results/Discussion

The review and evaluation of prior theoretical work, mathematical models, and experiments revealed that coiling of large-scale (vs. analytical scale) columns has been studied and reported by a small number of researchers. The most prolific, J. Calvin Giddings, in the 1960's, derived a mathematical model for the impact of coiled packed column dimensions on separation efficiency.[10,11,12,13,14] Tijssen in the 1970's also addressed coiling of chromatographic columns, but his work focused mainly on capillary and *open-tube analytical columns* and showed that coiling actually improved the resolution. However, both Giddings and Tijssen concluded that coiling and bending of *packed columns* decreases separation performance.[15,16,17]

The relationship developed by Giddings shows that coiling a packed column:
(1) increases the HETP (height equivalent to a theoretical plate) of the column, reducing the number of stages and therefore reducing the efficiency, and
(2) increases the negative impact of larger tube diameters.

$$H = \frac{7\, v r_0^4}{12 R_0^2\, \gamma D_g}$$

In this mathematical model, H or HETP is greatly dependent on the tube radius, r_0, as it is raised to the fourth power. The coil diameter, R_0, has an inverse and lesser effect, as it is only squared.

"Plate Theory" in Chromatography and HETP

In 1941, Martin and Synge worked out a method of describing and modeling chromatographic separations using a distillation analogy and terminology (where "column" is a literal vertical column and the "height equivalent to a theoretical plate – HETP" is the height of column needed for one stage of separation). "Column", "plate", and other distillation terms are still used today to describe chromatographic systems. HETP remains a key measure of column and packing performance.

$$HETP = \frac{Total\ column\ length}{Number\ of\ plates} \qquad \text{(smaller is more efficient)}$$

A. J. P. Martin and R. L. M. Synge, "A Theory of Chromatography", Biochem. J. 35 (1941) pp. 1358-1364. For this and a companion work, they were awarded a Nobel prize.

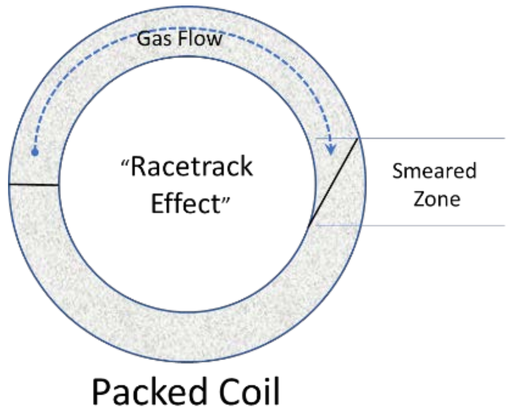

Figure 2: Illustration of the "Racetrack Effect" in coiled packed columns

A detailed review and reanalysis of data from the 2004 testing performed during this project revealed that column geometry played a large role in TCAP separation capability.

In 2004 tests were run on straight and coiled 2" diameter columns, but the results of the two cases were not compared at that time.[18,19] Reevaluation of the data revealed that the length per stage (same as HETP) increased by almost a factor of 2.5 for the coiled column, 4.3" vs. 1.6" for the straight column.

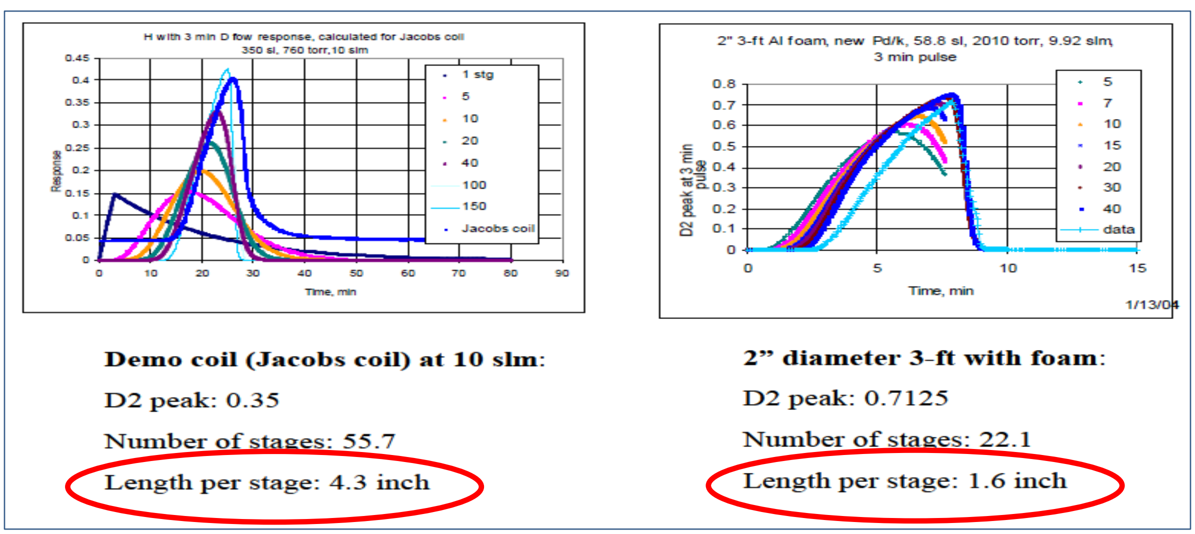

Figure 3: Comparison of coiled and straight 2" diameter column pulse tests showing an increase in HETP with coiling

Working with the Auburn University Center for Microfibrous Materials Manufacturing we determined that microfiber entrapped sorbents MFES made from copper microfibers and Pd/K could:

- Reduce or eliminate the wall-to-packing resistance to heat transfer
- Make the radial temperature profile of a column nearly isothermal
- Reduce wall effects on gas velocity
- Reduce axial dispersion and flatten concentration profiles across the column.[20,21,22,23]

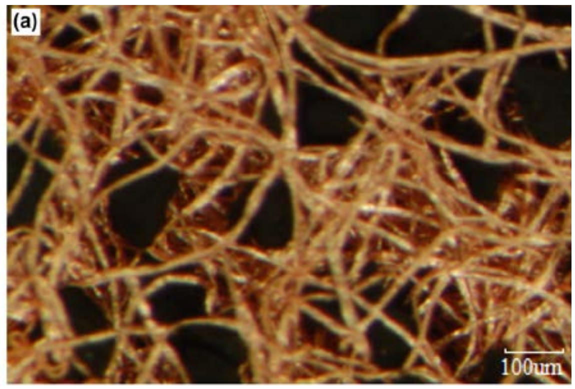

Figure 4: Microfibrous Entrapped Sorbent (MFES) using copper microfibers

FY2019 Accomplishments

- Discovered that coiling a packed column reduces separation efficiency compared to a straight column and amplifies the negative effect of increasing the tube diameter.
- Determined from prior SRNL testing that the data from straight and coiled packed column testing are consistent with the model showing low of separation efficiency with large diameter coils.
- Determined that MFES developed at Auburn University could improve TCAP performance by eliminating inhomogeneities such as channeling effects and by improving cycle time.

Future Directions

Apply report findings on column geometry, heat transfer, and MFES to a new design of test column for scale-up testing
Test new concepts for reducing the negative impact of column coils and bends.

FY 2019 Publications/Presentations

Presentation and paper at the April 2020 Technology of Fusion Energy (TOFE) meeting in Charleston, SC.

References

[1] M. W. Lee, "TCAP for Separation of Hydrogen Isotopes", USDOE Report DP-1660, also issued as Report No. DPST-83-82, 1983.
[2] M. W. Lee, "Information on TCAP Useful to the Preparation of a Disclosure", Report No. DPST-82-1047, 1982.
[3] Xin Xiao, L. Kit Heung and Henry T. Sessions, "Recent Advances in SRS on Hydrogen Isotope Separation Using Thermal Cycling Absorption Process", 2015, Fusion Science and Technology, 67:3, pp. 643-646.

[4] Anita S. Poore, "HT-TCAP Protium-Deuterium (HD) Test Summary, Part I", WSRC-TR-2004-00274, May 2004.

[5] Anita S. Poore, "Material and Process Characterization Testing Summary for HT-TCAP", WSRC-2004-00275, May 2004.

[6] James Chadwick, "A Palladium Column for Concentrating Tritium from 2-Litre Mixtures of Tritium and Hydrogen", U. K. Atomic Energy Authority Report, AERE 1/M47, 1958.

[7] E. Glueckauf and G. P. Kitt, "Gas Chromatographic Separations of Hydrogen Isotopes" in Vapour Phase Chromatography (D. H. Desty ed.), pp. 422-427, Butterworths Publications, Ltd., London, 1956.

[8] E. Glueckauf and G. P. Kitt, inventors, "Improvements in or Relating to Separation of the Isotopes of Hydrogen", Patent, GB825934A, filed 1956-02-04, published 1959-10-23.

[9] Carl O. Thomas and Hilton A. Smith, "Gas Chromatography with Hydrogen and Deuterium", J. Phys. Chem., 63, March 1959, pp. 427-431.

[10] J. Calvin Giddings, "Coiled Columns and Resolution in Gas Chromatography", Journal of Chromatography, 3 (1960) pp. 520-523.

[11] J. Calvin Giddings, "Nature of Gas Phase Mass Transfer in Gas Chromatography", Analytical Chemistry, Vol. 34, No. 10, September 1962, pp. 1186-1192.

[12] J. Calvin Giddings, "Principles of Column Performance in Large Scale Gas Chromatography", Journal of Chromatographic Science, Volume 1, Issue 1, January 1963, pp. 12–21.

[13] J. Calvin Giddings, "Plate Height in Coiled Columns", Journal of Chromatography, 16 (1964) pp. 444-447.

[14] J. Calvin Giddings, "Practical Criterion for Minimum Coil Diameter in Gas Chromatography", Analytical Chemistry, Vol. 37, No. 12, November 1965, pp. 1580-1581.

[15] R. Tijssen, "Effect of Column-Coiling on the Dispersion of Solutes in Gas Chromatography, Part I: Theory", Chromatographia, 3 (1970) pp. 525-531.

[16] R. Tijssen and R. T. Wittebrood, "Effect of Column-Coiling on the Dispersion of Solutes in Gas Chromatography, Part II: Generalized Theory", 5 (1972) pp. 286-295.

[17] R. Tijssen, "Axial Dispersion in Helically Coiled Open Columns for Chromatography", 1979, Technical University Delft, PhD Dissertation.

[18] L.K. Heung et al, "Hydrogen Isotope Exchange Tests in Support of HT-TCAP", WSRC-TR-2004-00402, 2004, Savannah River Site.

[19] L. K. Heung, G. C. Staack, J. E. Klein and W. D. Jacobs, "Tests of Isotopic Separation Efficiency of Palladium Packed Columns", Fusion Science and Technology, Vol. 54, Aug. 2008, pp. 391-394.

[20] Ranjeeth Reddy Kalluri, "Microfibrous Entrapper Catalysts and Sorbents: Microstructured Heterogeneous Contacting Systems with Enhanced Efficiency", 2008, Auburn University, PhD Dissertation.

[21] Min Sheng, Hongyun Yang, et. al., "Novel catalyst structures with enhanced heat transfer characteristics", Journal of Catalysis, 281, (2011), pp. 254–262.

[22] Min Sheng, Hongyun Yang, "High conductivity catalyst structures for applications in exothermic reactions", Applied Catalysis A: General, 445– 446, (2012), pp. 143– 152.

[23] Min Sheng, Donald R. Cahela, et. al., "Effective thermal conductivity and junction factor for sintered microfibrous materials", International Journal of Heat and Mass Transfer, 56, (2013), pp. 10–19.

Acronyms

MFES	Microfibrous Entrapped Sorbents
HETP	Height Equivalent to a Theoretical Plate
HT-TCAP	Hydrogen-Tritium Thermal Cycling Absorption Process
Pd/K	Palladium coated on kieselguhr (diatomaceous earth) – the column packing material used in SRNL TCAP
TCAP	Thermal Cycling Absorption Process