Operational Characterization of a Combined Electrolysis Catalytic Exchange Process

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Abstract

Many current CECE systems, which are used to extract harmful tritium from heavy water nuclear reactors, operate with inefficient alkaline electrolyzers that contain dangerous caustic chemicals. Thus the Hydrogen Isotope Branch at Chalk River Laboratories developed and integrated a safer and more efficient PEM electrolyzer to replace the alkaline electrolyzer. In this research, a bench-scale CECE system with a PEM type electrolyzer at Chalk River Laboratories was tested at LPCE column temperatures of 20°C, 40°C and 60°C to determine baseline operational parameters and conditions for optimal isotopic exchange. Increased operational temperature led to greater isotopic exchange across the PEM electrolyzer but not the LPCE column, an irregularity likely caused by an insufficient amount of catalyst in the column. Increased LPCE temperature also led to a decrease in overall system flow stability. Finally, the PEM electrolyzer voltage exhibited an unusual sharp rise throughout testing, indicating the membrane's susceptibility to damage if used without proper conditioning. Research conclusions will be taken into consideration in setting up a new bench-scale CECE process that more accurately models tritium extraction using a PEM electrolyzer.

Key Words

Combined Electrolysis Catalytic Exchange (CECE), Liquid Phase Catalytic Exchange (LPCE), Proton Exchange Membrane (PEM) electrolyzer, Isotopic Exchange.

Introduction

Tritium is infrequently created in heavy water reactors that use deuterium enriched water as a moderator to reach criticality.[1] Although the concentration of tritium is low, the nuclear industry is concerned with the safe extraction of the tritium to protect its workers. In order to achieve this, the Combined Electrolysis Catalytic Exchange (CECE) process was created. The CECE process uses an electrolyzer and a Liquid Phase Catalytic Exchange (LPCE) column to promote isotopic exchange and thus highly concentrate tritium in the liquid phase to be later extracted.

Many current CECE processes use alkaline electrolyzers.[2-4] Alkaline electrolyzers are plagued with a number of issues includ-

ing low current density, low pressure operation, and a need for a large inventory of caustic chemicals.[5] In this research, the team modelled a bench scale CECE-D process which uses a PEM cell instead of an alkaline electrolyzer and deuterium instead of tritium. The PEM cell electrolyzes water with a membrane that is selectively permeable to protons and thus eliminates issues present in alkaline electrolyzers.[6]

The primary objective was to test the operational parameters and isotopic exchange of the CECE-D process with a PEM cell at three different temperatures. The project results were needed to help determine appropriate baseline operational temperatures for a new bench scale CECE-T system at Chalk River Laboratories which will also use a PEM cell but circulate tritiated water instead of deuterated water to better model tritium extraction.

Materials and Methods

The bench scale CECE-D rig set-up is outlined in Figure 1. Before start up of the rig, a leak test using Snoop® Liquid Leak Detector was conducted and the system was purged with argon. Upon start up, the system was filled with 50% D2O and the LPCE jacket temperature was set using a NesLabs RTE -111 Circulating Chiller to 20°C, 40°C or 60°C. Once stable conditions were reached, gas samples were collected at SP-1, SP-2, SP-3 and SP-4 and analyzed through gas chromatography to calculate the separation factor of the electrolyzer and LPCE column. The separation factor functions as a measure of the isotopic exchange of deuterium into liquid phase water across the electrolyzer and LPCE column and is calcu-

$$\frac{\text{deuterium concentration in liquid} \times (1 - \text{deuterium concentration in gas})}{\text{deuterium concentration in gas} \times (1 - \text{deuterium concentration in liquid})}$$

temperature. Additional measurements such as system pressure, room temperature, recombiner temperature, gas flow and cell voltage were constantly recorded using a Keithley 2700 Digital Multimeter Data Acquisition System and Datalogging System.

The PEM cell electrolyzes heavy water to form deuterated hydrogen gas which passes through the LPCE column to perform isotopic exchange with heavy water. Purified hydrogen gas leaving the LPCE column recombines with oxygen, formed within the PEM cell, to produce water vapour. The water vapour is then channeled to the bottom of the LPCE column. In another loop, residual water travelling with oxygen from the PEM cell is separated and flows back to the PEM cell and the LPCE column for continued isotopic exchange. The sample ports for data analysis are indicated as SP-1 through 5.

Previous data collected at the Hydrogen Isotope Branch at CNL was used from 2014/06/04 to 2015/02/07. The data collected from 2015/06/18 to 2015/07/28 was part of this research study. The CECE-D rig was shut down for the time in-between and therefore no data was collected. Previous testing data shows that the cell voltage increased at a rate of 0.000040 volts/day from 2014/08/28 to 2015/02/07. Recent testing shows that the cell voltage increased at a rate of 0.0087 volts/day from 2015/07/13 to 2015/07/28. The increase in recent cell voltage is 2.2×10^4 % faster than it was during previous testing.

Figure 3: The effect of LPCE temperature on PEM cell and LPCE separation factor (separation factor mean ± 1 SD).

There was a significant increase in the cell separation factor at LPCE temperatures of 40 °C and 60 °C from the cell separation factor at 20 °C. There was also a significant decrease in the LPCE separation factor at LPCE temperatures of 40 °C and 60 °C from the LPE separation factor at 20 °C. *significant at $p < 0.05$; **significant at $p < 0.005$; ***significant at $p < 0.001$.

Figure 4: The effect of LPCE temperature on CECE-D gas flow (SLPM mean ± 1 SD)

The mean was calculated from data collected over a 24-hour period of CECE-D operation by the Keithley 2700 Digital Multimeter Data Acquisition System and Datalogging System. There is a noticeably larger error at 60 °C (± 0.517675 SLPM) than at 20 °C (± 0.098767) due to larger fluctuations in gas flow over the 24-hour period while running at 60 °C. There were also large amounts of water condensation in locations of the rig which should not contain liquid water at 60 °C, including the oxygen outlet of the oxygen separator, the gas flow differential pressure cells and the outlet of the recombiner. An airlock was also found in the water supply differential pressure cell at 60°C.

Discussion

PEM Electrolyzer

The recent increase in PEM cell voltage from 2015/07/13 to 2015/07/28 seen in PEM cell voltage change (2014/06/04-2015/07/28) (Figure 2) is 2.2×10^4 % faster than the cell voltage's natural tendency to rise seen in previous testing. A potential explanation for the steep increase in cell voltage is membrane damage. Membrane damage was likely caused by inadequate conditioning of

the membrane after the long period of disuse or between the changes in the LPCE column temperatures made throughout the testing period. This is particularly important as the PEM cell membrane is already known to be susceptible to damage through tritium exposure [7] and thus additional sources of damage must be avoided. Proper conditioning of the PEM electrolyzer should therefore not be overlooked in future testing of the CECE-T rig.

Isotopic Exchange

The effect of LPCE temperature on PEM cell and LPCE separation factor (Figure 3) shows a significant increase in the electrolyzer separation factor as LPCE column temperature is raised incrementally from 20 °C to 60 °C. Thus, an increase in the LPCE temperature led to an increase in the amount of deuterium stripped from the gas phase and concentrated in the liquid phase through the PEM electrolyzer. Interestingly, Figure 3 also shows that the LPCE column separation factor decreased significantly with increasing LPCE temperature. This signifies that an increase in temperature led to a higher concentration of deuterium in the gas phase and lower concentration in the liquid phase across the LPCE column. Thus the LPCE column appeared to have exhibited the opposite isotopic exchange temperature dependency seen in the PEM electrolyzer. The unexpected results may be explained by considering the flow of the CECE-D rig and the equilibrium of the isotopic exchange. The greater isotopic exchange exhibited by the electrolyzer led to a lower concentration of deuterium in the water flowing into the LPCE column. The shift in the equilibrium controlling isotopic exchange of deuterium into the liquid phase was not as great for the LPCE column as it was for the PEM electrolyzer though. Therefore, the LPCE column likely exchanged deuterium back into the gas phase to comply with its own equilibrium constant. Clearly, this is an unfavourable outcome as the purpose of the CECE system is to concentrate heavier isotopes in the liquid phase. Thus for future CECE-T testing, it is important to consider that higher LPCE temperatures do generally increase isotopic exchange, but the exchange of the LPCE column must be greater than that of the electrolyzer to produce increased isotopic exchange of the system as a whole. The increase in isotopic exchange for the LPCE column tested was unexpectedly low likely because there was insufficient catalyst in the column.

System Flow

The system flow became increasingly variable as the LPCE temperature increased, as seen in the effect of LPCE temperature on CECE-D gas flow (Figure 4). The gas flow was more variable likely because there was a significant build up of liquid water in a number of locations which should only contain gaseous elements throughout the rig at 60°C. These buildups of water likely contributed to an unexpected automatic shut down of the rig that occurred after running the CECE-D rig at 60°C for a few days. The water buildup prevents the proper flow of gas throughout the system, which can often cause a large decrease in the pressure of components of the rig, such as the recombiner. If the decrease falls below the pressure trip point, the rig is automatically shut down.

Thus, while higher temperature operation increases isotopic exchange, it appears to also increase the risk of system flow interruptions.

Conclusion

There are a number of operational parameters to consider before advancing with the bench scale CECE-T start-up. While CECE-D operation at higher temperatures leads to increased isotopic exchange, the isotopic exchange across the LPCE column must be higher than the exchange across the PEM electrolyzer or the LPCE column begins to downgrade the incoming water. Additionally, the benefit of greater isotopic exchange must be balanced with the increased risk of system flow variability at higher temperatures. The PEM electrolyzer should also be adequately conditioned to avoid the potential of membrane damage.

Future research should involve optimization of the bench scale CECE-T system with a PEM cell to better model PEM electrolyzer use in tritium extraction from heavy water reactors. Thus the viability of PEM cell use in the CECE process may be better assessed. Research on the bench scale CECE-T system should also explore the possibility for an industrial scale system which may help in the cleanup of tritiated water around the Fukushima incident site. The tritium contamination in the surrounding water of the Fukushima incident poses a potential risk to neighboring ecosystems [8] and thus is a pertinent issue that may be mitigated through the use of a CECE system. [9]

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REVIEW

by Dr. James Charbonneau

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In this paper the author performs an operational test of a process designed to promote isotopic exchange in nuclear reactors. The setup involves a new Proton Exchange Membrane electrolyzer along side a Liquid Phase Catalytic Exchange column that removes deuterium from a gas phase and concentrates it in a liquid phase. The goal is to determine some baseline operational characteristics of the process for use in later tests using tritium, rather than deuterium. The paper is generally of very high quality. The topic is very interesting, the science is good, and the writing is strong. However, I'm not sure the article is at an appropriate level for the audience of the journal. Additionally, there are some issues with the statistical conclusions of the paper, all of which I discuss below.

The following is a list of all my comments regarding the paper as they appear, rather than in order of importance.

1. The introduction could use a bit more explanation of the components and processes involved in the experiment, such as what an electrolyzer does, what isotopic exchange is, and what a LOCE column does. This would make the paper more accessible to a general science audience.
2. The separation equation should be its own line and use variable instead of whole sentences. The variables should be described in the text.
3. Figure 2. How are these rates calculated? If one takes the absolute voltage increase over each test period, then certainly there is a difference, but it seems like the slope between the first two data points in the "previous testing" period is similar to the slope calculated in the "recent testing" period. In the discussion this difference in voltage rates was ascribed to damage of the membrane. Was the membrane similarly damaged during the beginning of the 2014-06-04 trial period?
4. Figure 2. It's not clear to me that reporting percent increase in a useful metric. The rate numbers themselves are sufficient.
5. Figure 3. There is a large gap here in the description of the statistics. The method of determining these means is very unclear and warrants some description outside figure caption. How many trials went into calculating these means? How were the standard deviations calculated? The use of p-values here seems inappropriate. They indicate significance when the error bars clearly indicate that the 3 separation factors in the PEM cell aren't different (the error bars all have overlap). However, in the LPCE at 20 C is significantly different than the other two temperatures based on the error bars. P-values are less and less being accepted by journals as a measure of significance. Your analysis should rest on conclusions drawn from your error bars. You may find that using the standard deviation of the mean gives a more meaningful statistic and supports your conclusion that the separation factor is increasing with temperature. It all depends on how many trials you did.
6. Figure 4. Once again, due to the error bars we can't say that these flows are actually different. Are these standard deviations calculated from the set of measurements taken over the 24 hours? If so, how many trials went into it? The standard error of the mean might be better to plot. Thank you for not using p-values.
7. PEM electrolyzer discussion. The reason given for the anomalous increase in cell voltage is membrane damage. The author needs to explain why membrane damage would explain this. What is it about the damaged membrane that makes the voltage increase faster. Did the same thing happen at the beginning of the "previous testing" period where the slope is similar?
8. Isotopic exchange and system flow. These sections are genuinely wonderful. I think the statistics used to form these conclusions need to be tightened up, but this is a first rate interpretation of the data.

The work is very strong, and the author should be proud. However, extremely special care must be taken with these statistics. The failure to properly describe them, and the incorrect use of them, can result in serious difficulties getting a paper published. For instance, Nature asks their reviewers to be particularly thorough with their analysis of the statistics in a paper. In particular, there is a strong movement to reject p-values as an indicator of significance. I urge the author to read <http://fivethirtyeight.com/features/science-isnt-broken/> for a great example of the malleability of p-values.

I'd like to talk about the standard deviation of the mean (also called the standard error). The standard deviation of a set of data tells us that if we were to perform one more trial, there is a 68% chance that the value of the trial would fall within one standard deviation of the average of the trials already taken. The standard deviation of the mean is $SE = \sigma/\sqrt{N}$, where N is the number of trials performed and σ is the standard deviation of those trials. The standard deviation of the mean tells us that if we performed the trials N times again, there is a 68% chance that the mean of that data would fall within SE of your current mean. The author must decide if this is actually more appropriate for their paper. It makes error bars smaller, and is thus often abused in papers, so the author must justify that this is the appropriate statistic.