

A Temperature Swing Absorption Process for Hydrogen Isotope Separation in the Fusion Fuel Cycle

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Most Research is Me-Search

Beatrice Beebe

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Zusammenfassung

Der Brennstoffkreislauf eines Fusionskraftwerks besteht aus einer komplexen Verschaltung vieler Prozesseinheiten, welche die kontinuierliche Aufbereitung und Bereitstellung des Brennstoffs realisieren sollen. Hierbei handelt es sich um die schweren Wasserstoffisotope Deuterium und Tritium. Charakteristisch für den Fusionsbrennstoffkreislauf ist das enorme Rezyklierungsverhältnis von unverbrauchten Edukten, da nur etwa 0.5 bis 1 % des eingespeisten Feedstroms reagiert. Während die Bereitstellung von Deuterium keine Herausforderung darstellt, handelt es sich bei Tritium um ein radioaktives Element mit beschränkter ziviler Verfügbarkeit von ca. 25 bis 30 kg, welches im Betrieb erbrütet werden muss. Das Tritiuminventar im Brennstoffkreislauf ist daher, sowie aufgrund kerntechnischer Regulierung, so gering wie möglich zu halten, was die Technologieauswahl und Auslegung der Prozesseinheiten maßgeblich bestimmt.

Im Rahmen dieser Arbeit wird die Prozessentwicklung für das *Isotope Rebalancing and Protium Removal* (IRPR) System vorangetrieben. Diese Prozesseinheit dient im Brennstoffkreislauf des europäischen Fusionsdemonstrationskraftwerk EU-DEMO zur Bereitstellung eines äquimolaren Deuterium-Tritium-Gemisches, welches die effizienteste Energiegewinnung aus der D-T Fusionsreaktion ermöglicht. Darüber hinaus wird der Anreicherung von Protium (^1H Wasserstoffisotop) im rezyklierten Brennstoffstrom entgegengewirkt. Der Protium Anteil im Brennstoffkreislauf ist kritisch, da dieser ab einer Konzentration von mehr als 1 % zu Plasmainstabilitäten führt. Die unvermeidbaren Protiumquellen sind Ausgasprozesse der Stahloberfläche des Reaktors und deren Interaktion mit Neutronen. Das IRPR System wird mit einem gemischten Wasserstoffisotopenstrom gespeist. Dieser wird in zwei Produktströme getrennt, wobei einer mit schweren Isotopen Tritium und Deuterium angereichert ist und zum Reaktor zurückgeführt wird. Der zweite Produktstrom enthält den Großteil des zugeführten Protiums und wird nach der Rückgewinnung von Tritium Restspuren in folgenden Prozesseinheiten in die Umwelt abgegeben.

Eine vielversprechende Technologie zur Realisierung der beschriebenen Trennaufgabe ist ein semikontinuierliches *coupled inverse and normal metal hydride reaction* Temperaturwechselabsorptionsverfahren (CMH-TSA). Dabei wird die temperatur- und isotopenab-

hängige Hydridbildung von Metallen und Metalllegierungen ausgenutzt. Das bisherige Referenzverfahren *Thermal Cycling Absorption Process* basiert auf der Verwendung einer mit Palladium befüllten Absorptionskolonne, welche wiederholt temperaturinitiiert ein Wasserstoffisotopengemisch mit einer inerten Schüttgutkolonne austauscht. Aufgrund des hohen Tritiuminventars und der geringen Prozessdurchsätze, erfüllt dieses Verfahren jedoch nicht die Anforderungen an das EU-DEMO IRPR System. Die in dieser Arbeit vorgestellte Prozessoptimierung erweitert den Aufbau um eine zweite aktive Trennkolonne. Diese ist mit einem metallischen Absorptionsmaterial befüllt, welches im Vergleich zu Palladium einen entgegengesetzten Isotopeneffekt bei der Hydridbildung aufweist. Die Interaktion der beiden aktiven Trennkolonnen ermöglicht einen reduzierten Energieverbrauch durch optimierte Prozesstemperaturen, verringert das Tritiuminventar und erhöht den Systemdurchsatz sowie die Wertproduktkonzentration in den Produktströmen.

Zunächst wurden dafür mit Hilfe von experimentellen Wasserstoffabsorptionsstudien Legierungen hinsichtlich ihres Isotopeneffektes und ihrer Sorptionscharakteristiken bei der Hydridbildung untersucht. Diese ermöglichten die Identifizierung einer geeigneten TiMn Legierung als Partnermaterial zur bestehenden Palladium-Füllung. Im nächsten Schritt wurden Protium-Deuterium-Trennversuche im Labormaßstab durchgeführt. Diese dienten, neben der Untersuchung verschiedener Prozessführungen, zur Charakterisierung der Trenneffizienz der Einzelkolonnen, sowie deren Optimierung durch den kombinierten Betrieb. Die Prozessentwicklung wurde darüber hinaus unterstützt durch ein entwickeltes, eindimensionales, transientes und rigoroses CMH-TSA Prozessmodell. Die erforderlichen Modellparameter wurden auf Basis der experimentellen Daten implementiert und für tritiumhaltige Spezies extrapoliert. Sowohl die Versuche zur Materialcharakterisierung, als auch die Separationsexperimente dienten zur Modellvalidierung.

Mit Hilfe des validierten CMH-TSA Modells wurden die Absorptionskolonnen für das EU-DEMO IRPR System dimensioniert und eine optimierte Prozessführung unter kontinuierlichem Gasaustausch hergeleitet. Dabei konnte gezeigt werden, dass die Verwendung einer zweiten Trennkolonne die Produktentnahme bei tiefen Temperaturen ermöglicht, wodurch der Trennfaktor maximiert wird. Ein Scale-up des Prozesses erfolgt durch Parallelisierung der vorgeschlagenen Kolonnengeometrie. Die gezeigten Ergebnisse legen nahe, dass durch den CMH-TSA Prozess das Tritiuminventar signifikant reduziert wird und die Technologie für die Trennaufgabe des IRPR Systems geeignet ist.

Abstract

The fuel cycle of a fusion power plant is a complex network of various process units, which continuously condition and supply the fuel. This consists of the heavy hydrogen isotopes deuterium and tritium. Characteristic for fusion fuel cycle is the high recycling ratio of unburnt fuel, since only around 0.5 to 1 % of the feed stream reacts. While providing sufficient deuterium is not challenging, tritium is a radioactive element with limited civilian availability of around 25 to 30 kg, which therefore has to be created artificially during operation. For this reason, and due to nuclear regulations, the tritium inventory in the fuel cycle must be kept as low as possible, which is the main design driver and technology selection criteria for the process units.

This work contributes to the process development of the Isotope Rebalancing and Protium Removal (IRPR) system. The fuel cycle of the European fusion demonstration power plant (EU-DEMO) foresees this process unit to re-establish an equimolar deuterium-to-tritium-ratio, which allows for the most efficient energy production from the D-T fusion reaction. Additionally, the IRPR system counteracts the protium built-up within the recycled fuel stream. The proportion of protium (^1H isotope) in the fuel cycle is critical, as concentrations of more than 1 % lead to plasma instabilities. Protium inevitable enters the fuel cycle due to outgassing processes of the reactor steel surface and its interaction with neutrons. The IRPR system is fed with a mixed hydrogen isotope stream, which is separated into two product streams of contrary isotope composition. The product stream enriched in the heavy isotopes tritium and deuterium is routed to the reactor. The second product stream contains most of the supplied protium and is released to the environment after recovering residual tritium species in subsequent process units.

A promising technology to realize this separation task is a semi-continuous coupled inverse and normal metal hydride reaction temperature cycling absorption (CMH-TSA) process. CMH-TSA exploits the temperature- and isotope-dependent formation of metal hydrides. The state-of-the-art Thermal Cycling Absorption Process (TCAP) uses a palladium-filled absorption column which temperature-initiated repeatedly exchanges a hydrogen isotope mixture with an inert plug flow reverser column. However, due to its high tritium in-

ventory and low system throughput, this process does not fulfil the requirements for the EU-DEMO IRPR system. The process optimization presented in this thesis extends the reference process by a second active separation column. This column is filled with a metallic absorption material, which has an opposite isotope effect on its hydride formation compared to palladium. The interaction between both active separation columns enables reduced energy consumption through optimised process temperatures, reduces the tritium inventory, and increases the system throughput and value product concentration in the product streams.

First, experimental hydrogen absorption studies were performed to investigate the isotope effect and sorption characteristics of alloys during their hydride formation. These allowed for the identification of a suitable TiMn alloy to be paired with palladium in the CMH-TSA process. Next, protium-deuterium separation experiments were performed in a laboratory set-up, to investigate the separation efficiency of a single column, as well as the optimization through combined column operation. Beside, variations in the process operation were explored. In addition, the process design was supported by developing a rigorous, transient, one-dimensional CMH-TSA process model. The required model parameters were derived from the experimental data and extrapolated for tritium-containing species. The material characterisation tests and the separation experiments served to validate the model.

Using the validated CMH-TSA model, the absorption columns for the EU-DEMO IRPR system were sized and an optimized process operation exploiting continuous gas exchange was identified. Furthermore, product extraction at low temperatures was demonstrated, which maximises the separation factor, and is enabled by the combination of two active absorption columns. The process scale-up is realized by parallelisation of the proposed column pair design. The results indicate that the developed CMH-TSA process significantly reduces the tritium inventory, thus demonstrating the suitability of CMH-TSA technology for performing the separation task of the IRPR system.

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Chapter 1

Introduction to Fusion Energy and Motivation

Energy production by fusion energy recently experienced increasing public attention due to a successful laser based fusion experiment reported by the *National Ignition Facility* in the US, demonstrating a net energy gain [1]. Governmental interest and support for the development of commercial fusion power plants as well as investments in private start-ups currently rapidly grow, leading to a boost in fusion technology research [2, 3, 4]. However, researchers have been investigating the potential of an energy source exploiting the fusion of light atoms for decades. Arthur Edington can be seen as the first fusion energy pioneer, who recognised the fusion reaction of hydrogen to be the source of power of stars in the 1920s [5, 6]. Since then, the transfer of this almost inexhaustible source of energy into a controllable nuclear power plant technology has been envisioned and researched intensively. The technical realization is challenging, due to the extreme conditions which are required to sustain fusion reactions. Nonetheless, since the energy demand of the world population is continuously growing and the awareness of climate change increases, society is searching for sustainable, renewable and carbon emission-free energy solutions to which fusion technology can contribute.

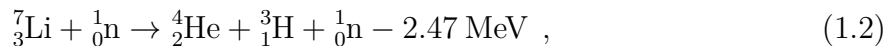
Fusion technology exploits the energy release occurring during the merging of light atoms whose nuclear mass is smaller than those of the most stable element $^{56}_{26}\text{Fe}$. In fact, the total mass of a fused nucleus is smaller than the sum of the mass of all initial fusing nuclei. This effect is known as mass-defect. The on the first glance lost mass is transformed into energy, which is described by Einstein's famous formula $E = mc_{\text{light}}^2$, stating that energy and mass are equivalents [7]. In there, the conversion factor between the motionless mass m and the energy E equals the square of the speed of light c_{light} . To overcome Coulombs repulsion of nuclei and trigger their fusion, extreme kinetic energies of $\sim 8.62\text{keV}$ are

necessary, at which matter is present in a plasma state. In fusion reactors using a magnetic confinement to control the fusion plasma, magnetic fields protect the reactor wall from damage by plasma contact. Two magnetic confinement reactor concepts exist: a *stellarator* and a *tokamak*. The former can be operated continuously as the poloidal magnetic field is completely created from surrounding external magnetic field coils. In contrast, within a tokamak, the plasma current, which is induced by a central solenoid, contributes itself to the magnetic confinement. For this, the central solenoid current is continuously ramped-up, comparable to a transformer, until it reaches its upper limit. Then a reset to initial state follows. Therefore, plasma operations in *tokamaks* are pulsed. A second magnetic field completes the confinement by external poloidal and toroidal coils.

The probability of two particles to fuse is highly dependent on their kinetic energy and thus the temperature. A common term for this relation is *cross-section*. The most promising, feasible fusion reaction concerning its technical realisation on earth, due to its high cross-section at comparable low plasma temperatures [8], is the merging of the heavy hydrogen isotopes tritium $\text{H}_1^3 = \text{T}$ and deuterium $\text{H}_1^2 = \text{D}$ (hereafter referred to as *fuel*):



The fusion products of this reaction are a helium nucleus (hereafter referred to as *ash*) and a fast neutron. This neutron is unaffected by the magnetic field lines, thus its kinetic energy and the heat provided by its deceleration in the *blanket* is used to operate a power cycle, which allows for energy generation. While deuterium is a stable and abundant isotope for example present in seawater, tritium is a rare and radioactive element (half-life time of ~ 12.3 years). Its natural formation by the reaction of upper atmosphere nitrogen atoms with cosmic ray neutrons (natural inventory of ~ 1.8 kg) [9, 10] and artificial creation as by-product in Canadian Deuterium Uranium (CANDU) nuclear reactors (production rate ~ 2 kg per year [11]) is not sufficient to supply fusion plants. Therefore, it needs to be generated during plasma operation, which is envisioned by the aforementioned *breeding blankets* [12]. This technology allows for tritium breeding due to nuclear reactions of ${}^7_3\text{Li}$, ${}^6_3\text{Li}$ and neutrons [13]:



To maintain a burning plasma, i.e., the fusion reaction, a fusion power plant requires a closed and self-sufficient fuel cycle, which continuously supplies the torus, i.e., the plasma chamber, with the appropriate amount and composition of fuel. Hereby, the fusion fuel

cycle is characterised by its enormous recycle ratio of unburnt fuel, as in fact only 0.5 to 1 % of the torus feed stream is burnt (meaning reacting to He-ash). Thus, in addition the artificial breeding of T and the supply of fuel, the fusion fuel cycle has to fulfil several separation and purification tasks. A network of interacting systems perform these process operations, forming the fuel cycle.

This work contributes to the technology development for the *European Demonstration Power Plant* (EU-DEMO) fuel cycle, which is introduced in the following.

1.1 The EU-DEMO Fuel Cycle

The EU-DEMO exploits a tokamak reactor chamber and shall produce up to 500 MW net-electricity, serving as scale-up step towards a commercial fusion power plant [14, 15]. The development of the EU-DEMO fuel cycle focuses on the identification and selection of suitable technologies for the various process units and their advancement to higher technical readiness levels. Many of these investigated technologies are first of their kind due to the novelty of application. The main design driver of the fuel cycle and its units is to reduce the tritium inventory for safety and economic reasons as well as governmental nuclear regulation [16, 17]. For EU-DEMO, these design requirements are targeted by utilizing a three-loop-architecture for its fuel cycle. This concept allows to operate systems with high tritium throughputs at short residence times. Furthermore, as each system does not process the total torus exhaust gas stream, the required system size can be reduced, which optimizes the fuel cycles scalability. [18] A simplified block diagram of the EU-DEMO fuel cycle and its process units is shown in Figure 1.1.

Most of the unburnt fuel is recycled directly via the *Direct Internal Recycling Loop* (DIRL), significantly reducing the tritium inventory. This stream equals 80 % of the plasma exhaust gas stream and is only composed of hydrogen isotopologue species. The remaining proportion, which contains hydrogen species, the helium-ash, plasma enhancement gases (PEGs) and other impurities like tritiated water (Q_2O), is processed towards the *Inner Tritium Plant Loop* (INTL). In this loop, helium and impurities are separated within the *Exhaust Processing System* (EPS). The pure hydrogen stream is then routed to the *Isotope Rebalancing and Protium Removal* (IRPR) system, which supports the re-adjustment of the optimal equimolar fuel composition and withdraws protium impurities. The second process stream of the EPS which only contains traces of tritium beside ash and further impurities in various chemical forms is routed to the *Outer Tritium Plant Loop* (OUTL). This loop processes all streams with low tritium content and is additionally fed with exhaust streams from gloveboxes, the air ventilation system of the tritium plant, the coolant stream and flush gas which are routed through the breeding blanket. In the OUTL, the process streams are detritiated by the *Water Detritiation* and *Exhaust Detri-*

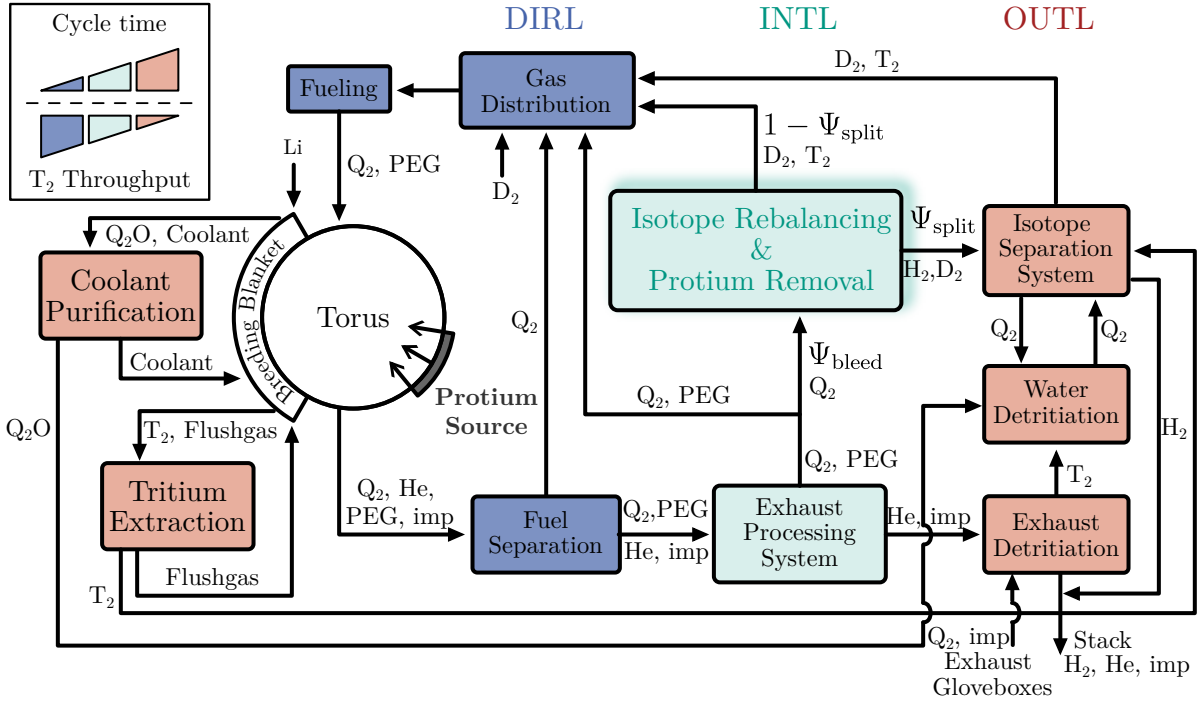


Figure 1.1: Simplified fuel cycle architecture of the European Demonstration Power Plant, which is built from various interacting process units. The fuel cycle supplies the D-T fusion reaction within the torus with fuel and plasma enhancement gases (PEGs) and processes the torus exhaust gas stream. This work contributes to the technology development of the highlighted Isotope Rebalance and Protium Removal system. This system processes a bleed stream fraction of Ψ_{bleed} of the total fuelling rate and provides two product streams which are contrary enriched in their hydrogen isotope composition. A fraction Ψ_{split} of the IRPR system throughput is routed to the OUTL, to strip protium from the recycled fuel stream. Protium impurities cause plasma instabilities and inevitable enter the fuel cycle due to outgassing processes and neutron-wall-interactions.

tiation units before being discharged to the environment through the stack. For a detailed introduction to all specific functionalities and system technologies the reader is referred to [18, 19]. This work contributes to the technology evaluation and development of the IRPR system, which necessity and requirements are described in detail in Section 1.2.

1.2 Isotope Rebalancing and Protium Removal System

The task of the IRPR system, located within the INTL, is to establish the specified fuel composition, i.e., the tritium-to-deuterium ratio, and to counteract the protium (lightest hydrogen isotope ^1H) built-up within the fuel. A protium fuel content exceeding molar proportions of approximately 1% causes plasma instabilities [17, 18]. It enters the fuel cycle due to inevitable outgassing processes of the plasma vacuum vessel surface and nuclear reactions between neutrons and the wall [20]. To the current point of knowledge,

the absolute protium source term is not known and may vary over the plants life time [18]. As protium is not burnt by the fusion reaction, it continuously dilutes the recycled fuel stream.

Fulfilling these tasks require a technology that continuously processes a mixed hydrogen isotope stream provided by the EPS, and produces two enriched product streams of contrary composition of isotopes. By avoiding a complete separation into H, D and T, the unnecessary separation work of the educts D and T is reduced. The product stream enriched in heavy isotopes is routed to the *Gas Distribution System* (GDS) and contains the value products tritium and deuterium. In contrast, the second product stream contains most of the supplied protium and is processed to the *Outer Tritium Loop* (OUTL), where it is fed to the *Isotope Separation System* (ISS).

To size the system throughput of the IRPR unit, the separation task and protium imbalance need to be defined. Contributors to deuterium imbalances are plasma transport and isotope effects during pumping, while protium imbalances occur from outgassing processes as mentioned before.

The necessary bleed stream fraction Ψ_{bleed} of the total torus throughput $\dot{N}_{\text{torus}}$ to counteract the up-built of protium follows from a protium balance

$$\Psi_{\text{bleed}} = \left(\frac{\Delta \dot{N}_{\text{H}_2}}{z_{\text{H}_2, \text{max}}^{\text{G}} \dot{N}_{\text{torus}} + \Delta \dot{N}_{\text{H}_2}} \right), \quad (1.4)$$

where $\Delta \dot{N}_{\text{H}_2}$ equals the imbalance of protium produced by a source term and $z_{\text{H}_2, \text{max}}^{\text{G}}$ is the tolerated molar protium fraction in the total throughput. For the current EU-DEMO fuel cycle design, $\dot{N}_{\text{torus}}$ equals 380 to 430 Pam³/s¹ and the maximum tolerable molar protium fraction in the fuel is limited to 1 %. This leads to a required bleed stream fraction of ~ 2.5 % of the total throughput, assuming a protium source term of 0.1 Pam³/s. [22, 18] Therefore, a minimal flow of 11 Pam³/s has to be processed by the IRPR system, which equals to 13 % of the total inner loop throughput, assuming a close to ideal separation efficiency.

¹The unit Pam³/s corresponds to pressure-volume flow rate $p \cdot \dot{V}$ at a reference temperature $T = 273.15$ K and is typically used to express throughputs in vacuum systems. From this definition it follows that 1 Pam³/s equals $4.4 \cdot 10^{-4}$ mol/s. A detailed description of resulting EU-DEMO Tritium Plant dimensions and the piping system can be found in [21].

1.2.1 Requirements and Technology Selection for IRPR

The separation technology for the IRPR system faces several constraints:

- The operational tritium inventory has to be as low as reasonably achievable. This also includes a process pressure limit of 5 bar.
- Unnecessary separation shall be minimized since tritium and deuterium are re-mixed before being fuelled.
- Energy intense cryogenic process temperature shall be avoided. A lower limit of -10 °C is envisioned.
- A (semi-)continuous operation has to be possible, whose process time integrates into the fuel cycle dynamics.
- A safe and non-hazardous operation is required.

The IRPR system functionality requires a technology, which is capable to separate hydrogen isotopologue species from each other, exploiting an isotope effect in the underlying separation principle. Isotope effects are caused by the mass difference between the isotope species and can be distinguished for example in physical or chemical effects, but also in kinetic and thermodynamic effects. [23, 24] The existence of chemical and reaction kinetic isotope effects initially seems surprising, as isotopes are in general considered identical in their chemical behaviour due to their identical electron shells. However, the reaction kinetics are influenced by the deviation in the atomic masses, which are very distinct for hydrogen isotopes. Table 1.1 classifies technologies for hydrogen isotope separation and the corresponding isotope dependent characteristic for separation.

A technology assessment of possible candidates revealed a *Temperature Swing Absorption* (TSA) process to be the most promising technology candidate to fulfil the IRPR systems task [26, 27] due to the following reasons: While cryo distillation [28] and molecular sieves operate at cryogenic temperatures, separate into single species and exhibit high tritium inventories, membrane technologies [29] and gas centrifuges [25, 30] require multiple stages due to the limited separation efficiency. In addition, their maximum system throughputs are low. Temperature Swing Absorption (TSA) and Pressure Swing Absorption (PSA) have the potential to overcome the above mentioned deficiencies. They transform the batch process of gas chromatography [31, 32] into a semi-continuous operation, which exploits hydrogen isotope dependent metal hydride formation. The affinity of a metal or alloy to react either to a light or heavy hydride is a material characteristic. For example palladium preferably reacts with light isotopes, which is referred to as *normal* isotope effect. Materials having an affinity to form heavy hydrides show an *inverse* isotope effect (detailed in Subsec. 2.1.3). While the process is controlled by adapting the operation

Table 1.1: Overview of hydrogen isotope separation technologies, the corresponding characteristic showing an isotope effect and the separation principle classification [23, 25, 24].

separation technology	separation principle	isotope dependent characteristic
cryo distillation	thermodynamic	vapour pressure
membrane	physical-kinetic	diffusion velocity
molecular sieve	thermodynamic	adsorption
gas centrifuge	physical	molecular weight
gas chromatography	chemical-kinetic	metal hydride formation
temperature swing absorption	chemical-kinetic	metal hydride formation
pressure swing absorption	chemical-kinetic	metal hydride formation

temperatures in the case of TSA, PSA defines the process pressures instead [33]. The latter requires elevated process pressures in order to completely utilise the absorption capability of the metal packings, causing higher tritium inventories in comparison to TSA operation, which is therefore preferred. For a more detailed description of the respective technology disadvantages and the reasons for being excluded for the IRPR application it is referred to the predecessor work by Neugebauer (process conceptualisation) [26], where the complete technology assessment summary is given.

1.3 Objective and Structure of Work

Objective of this thesis is to develop an optimized TSA process, serving as technology for the IRPR system within the EU-DEMO fuel cycle. This also includes its upscaling for the current EU-DEMO design point. The state-of-the-art *Thermal Cycling Absorption Process* (TCAP) developed by Savannah River National Laboratories is used for reference [34, 35, 36], to evaluate proposed process adaptations concerning optimized separation efficiency and operation temperatures and pressures. The original TCAP is set-up by a single active separation column, exploiting the isotope dependent metal hydride formation of palladium, and an inert plug flow reverser column. Although TCAP demonstrate promising separation efficiencies, it cannot satisfy the requirements for the IRPR system, due to its high tritium inventories and limited system throughputs. Therefore, an optimized TSA process, the *coupled inverse and normal metal hydride reaction temperature swing absorption* (CMH-TSA) process, is investigated in this work. It differs from TCAP by implementing a second active separation column, filled with a metallic packing, showing

an opposite, i.e., inverse, isotope effect to its hydride formation than palladium. Detailed process descriptions and differences of TCAP and CMH-TSA are given in Section 2.2. In the following, research hypotheses are stated, which serve as guide for the CMH-TSA process development pathway throughout this thesis.

Hypothesis 1 (H1)

The fuel separation and conditioning task of the EU-DEMO IRPR system can be performed using a TSA process.

Hypothesis 2 (H2)

Established TSA processes, like the TCAP, are optimized with respect to product enrichment and system throughput by coupling a packed palladium column with a second packed separation column. The metallic packing in this second column shows an opposite isotope preference in its hydride formation to palladium, allowing for the operation of a CMH-TSA process.

Hypothesis 3 (H3)

There exists an absorption material (metal or alloy), which has an inverse isotope effect of hydride formation and whose metal-hydrogen-interactions are in the order of magnitude to those of the palladium-hydrogen-system.

Hypothesis 4 (H4)

The proposed CMH-TSA process is sufficiently efficient and economical, such that it provides the base for large-scale application in future commercial fusion power plants.

Structure of Work

In Chapter 2 the fundamentals of metal-hydrogen-interactions and the material characteristic isotope effect during metal hydride formation are explained. Then the state-of-the-art TCAP is introduced and the potential of the CMH-TSA process developed in this work is differentiated. The chapter ends with an overview of promising material candidates for CMH-TSA application.

Chapter 3 presents the manufacturing of the selected candidates, characterisation methods and the experimental results, which allow for the identification of a suitable material to be paired with palladium.

H₂-D₂ separation experiments (discussed in chapter 4) using the selected material couple demonstrate the separation capability of the CMH-TSA process, enable investigations of different operation procedures and deliver validation data for the CMH-TSA process model, which is presented in Chapter 5. To enable a process scale-up for IRPR application, the model is extrapolated to tritium operation.

In Chapter 6 the developed model is used to identify a CMH-TSA unit design and investigate an optimized process operation mode, which follows from the results of the previous chapters. In addition, the required IRPR system size for EU-DEMO, exploiting the developed CMH-TSA process, is given.

Chapter 7 points out recommendations for future process and material development steps.

Chapter 2

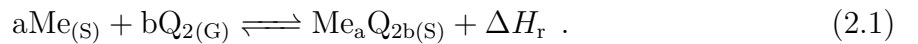
Fundamentals

2.1 Metal Hydrogen Interactions

The separation effect of a TSA process is based on isotope dependent metal hydride formation of the chemisorbing packing material. Therefore, the underlying fundamentals of metal hydrogen interactions during this heterogeneous reaction are described in the following. This includes presenting the general metal hydride reaction, the physical background of the isotope effect of hydride formation for certain metals or alloys and the measurable characteristics which serve as figure of merit to quantify the isotope effect.

2.1.1 Reaction of Metal Hydride Formation

Metals and their alloys exhibit the capability of reversibly reacting with the various hydrogen isotopes Q to a metal hydride. The resulting stoichiometry or crystal structures of the corresponding hydride are material characteristic and depend on several factors such as the metal lattice, the alloy composition or the amount of absorbed hydrogen. The heterogeneous metal hydride reaction is formulated by



Any hydrogen isotopologue molecule Q_2 ($\text{Q}_2 = \text{H}_2, \text{HD}, \text{HT}, \text{D}_2, \text{DT}$ or T_2) dissociates on the metal surface Me and forms the metal hydride Me_aQ_{2b} . For most metal hydrogen systems the hydride formation is an exothermal process expressed by the reaction enthalpy ΔH_r and is called absorption. The reversed reaction is denoted as desorption, thus an endothermal dehydrogenation process, where emerging Q atoms recombine on the metal surface to Q_2 molecules and diffuse to the surrounding gas phase. [37, 38, 39]

To enable the reversible uptake of hydrogen, usually a metal or alloy requires a pre-treatment called *activation*. The metallic surface is covered with an oxide layer of various thickness, depending of the materials' manufacturing process. An activation procedure is a necessary surface conditioning that cracks the oxygen layer on the metal surface, which inhibits the absorption process as it acts as hydrogen barrier. The activation treatment includes high hydrogen pressure (mechanical stress) and high temperatures (thermal stress). During a typical activation procedure, first the metal is exposed to a high pressure hydrogen atmosphere above the corresponding equilibrium pressure to force hydrogen through the inert layer. Elevated temperatures support this process, as the hydrogen diffusion is enhanced. Second, a holding time at elevated temperature follows to completely release absorbed hydrogen. Those two steps are repeated several times, hence the material is repeatedly hydrided and dehydrided (*cycling*). During this cycling the introduced stresses by the lattice expansion during hydride formation cause decrepitation, i.e., self-pulverization of the absorption material. Thereby, fresh metallic surface is exposed which uninhibited reacts with hydrogen. To obtain reproducible absorption behavior, it is essential to repeat the cycling until the equilibrium alloy grain size is reached, which typically equals a particle size of 5 to 15 μm . Otherwise the particle surface further changes during processing, influencing the reaction kinetic and establishing equilibrium pressures. [40, 37, 41]

After completed activation, fresh metallic surfaces are highly reactive and therefore sensitive for contamination or competing reactions. Especially the contact with oxygen species has to be avoided as they trigger metal oxide formation. Metal oxide layers inhibit hydrogen uptake and thus suppress metal hydride formation. In the case of intermetallic compounds this metal oxide formation can be critical. For example titanium alloys oxidize almost irreversible which causes the loss of hydrogen absorption capability. Besides poisoning of metallic absorption material, the metal oxygen reaction is a severe safety concern. The formation of metal oxide is a highly exothermal reaction. If a metal is hydrided and a oxide formation occurs, the heat release immediately causes hydrogen emerging from the lattice risking an oxyhydrogen reaction.

2.1.2 Pressure-Concentration-Isotherms

Thermodynamically the metal hydride formation is characterised by different phases of the binary hydrogen-metal system. These can be differentiated using a pressure-concentration-isotherm¹ (PCI), where the establishing equilibrium pressure $p_{\text{eq,Q}_2}$ in the gas phase is related to the molar ratio of absorbed hydrogen n_{Q} to metal amount n_{mat} , which is

¹Another term used in literature is pressure-*composition*-isotherm.

defined as concentration² c for a system temperature T . An ideal PCI is schematically shown in Figure 2.1. The amount of absorbed hydrogen follows from

$$c = \frac{n_Q}{n_{\text{mat}}} . \quad (2.2)$$

In the α -Phase, the absorbed hydrogen is dissolved between the metal atoms in the interstitial gaps (solid solution phase) while the metal lattice structure is not impacted. This phase occurs for small concentrations of absorbed hydrogen and is characterized by a steep increase of the equilibrium pressure for increasing c . The establishing equilibrium pressure follows from Sieverts' law which is equivalent to Henry's law for binary dissociating solution where

$$c = K_{\text{SV}} \sqrt{p_{\text{eq}, Q_2}} \quad (2.3)$$

gives a square root dependency of c to p_{eq, Q_2} with the material dependent Sieverts' constant K_{SV} [42].

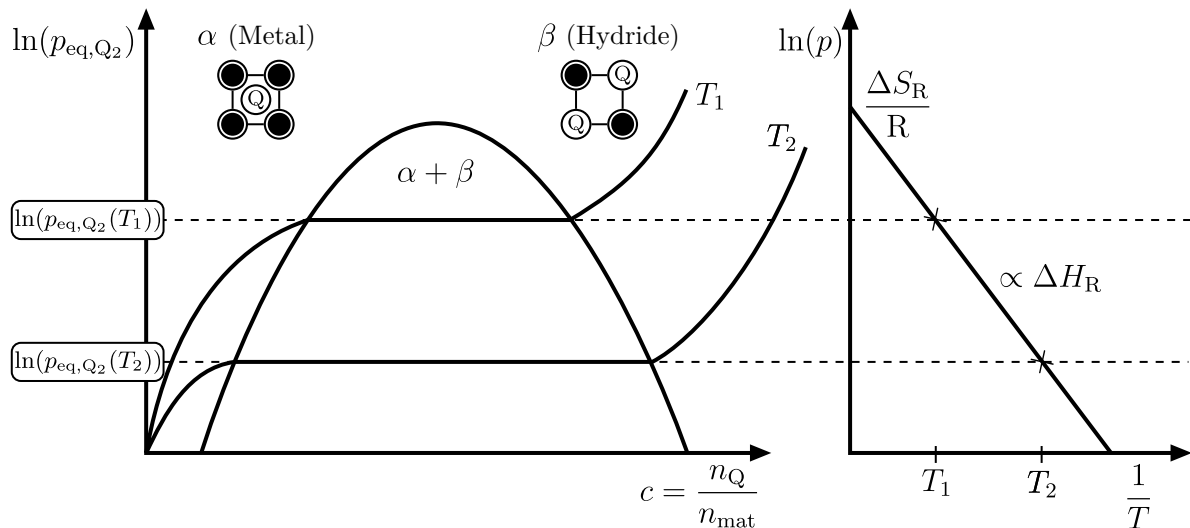


Figure 2.1: Left: Schematic ideal pressure-concentration-isotherm of a metal hydride system forming α - and β - phases dependent on the concentration c of absorbed hydrogen in the metal lattice. Right: Schematic van't Hoff plot derived from several PCI for a metal hydride system, correlating the plateau-pressure to the system temperature.

If the maximum solution concentration in the α -phase is reached nucleation starts and a hydride phase (β -phase) begins to form. In the β -phase the absorbed hydrogen atoms occupy regular metal lattice places. At this point the system consists of three phases namely the α - and the β -phases and gaseous hydrogen. According to Gibbs' Phase rule only one degree of freedom remains, therefore, for an ideal system, the equilibrium pressure p_{eq, Q_2} remains constant for increasing concentration c . This transition region where the α - and

²From the definition the term *loading* would be more suitable. However, in literature the utilization of *concentration* is common and therefore used throughout this thesis.

the β -phase coexist is defined as $\alpha - \beta$ -region or *plateau*-region. However, in real systems and alloys the plateau-pressure often exhibits a slope. This is caused by the overlap of varying equilibrium pressures of different material compositions due to inhomogeneous lattices, which may occur in non-eutectic alloys [37, 43]. Also defects in the lattice, contaminated surfaces and stresses are reasons for an obtained sloping-plateau [44, 45, 46, 40]. Another effect that can be observed in real metal-hydrogen-systems is the *gas hysteresis*. When measuring a PCI for absorption and desorption, different equilibrium pressures are obtained. In general equilibrium pressures of absorption are higher than the corresponding equilibrium pressure of desorption. This deviation results from stresses induced in the lattice during absorption which lead to plastic and elastic deformation. Since the desorption equilibrium pressure can be more reliably reproduced, it is considered to be the "real" equilibrium while the absorption pressure is denoted as meta-stable [37, 47, 39]. Completed hydrogenation is accompanied by an exponential pressure increase for further uptake of hydrogen.

The plateau-region is of interest for technical metal hydride applications, as it represents the technical operational range. It is also referred to as reversible capacity of a hydrogen storage material [41, 37]. In general, the equilibrium pressure increases with increasing system temperature ($c = \text{const.}$). Meanwhile lower temperatures exhibit higher capacities. Its dependence of the systems temperature T is expressed by the *van't Hoff* equation

$$\ln\left(\frac{p_{\text{eq}, Q_2}}{p_0}\right) = \frac{\Delta H_R}{RT} - \frac{\Delta S_R}{R} \quad , \quad (2.4)$$

where ΔH_R is the enthalpy of hydride formation, ΔS_R is the entropy of hydride formation and R the ideal gas constant. The *van't Hoff* diagram correlates the plateau-pressure dependence on the system's temperature (c.f. Fig. 2.1, right). From the measurement data of several PCI at various temperatures, the diagram can be obtained. Inhere, the intersection of the revealing line gives the value of $\frac{\Delta S_R}{R}$ while the slope contains the value of ΔH_R . [39]

PCI are crucial for the determination of the isotope effect of the hydride reaction and the evaluation whether the absorption characteristics are within the operation range of the TSA process. For metals having an isotope effect, the resulting PCI for the H_2 -Me and D_2 -Me system differ from each other for equal c and T conditions. The favored isotope is characterized by the PCI showing lower pressures and a higher capacity over the whole concentration range. In addition, the described deviations in the obtained equilibrium pressures lead to different plateau-pressure-temperature dependences given in the van't Hoff diagram. Thus the line of the preferred Q_2 -Me system is positioned below the lines

obtained for the other Q_2 -Me systems. In the following the definition and the physical origin of the isotope effect is described in more detail.

2.1.3 Isotope Effect of Metal Hydride Formation

Certain metals and alloys show an isotope preference when forming their hydride according to the reaction given in Eq. (2.1) [48, 49, 50]. Depending on the affinity either a metal protide, metal deuteride or metal tritide is preferably formed. This thermodynamic isotope effect is explained schematically in Figure 2.2. Here the zero-point vibrational energies of Q_2 molecules in the gas phase and Q atoms in the solid phase are shown, which can be understood as residual energy amount that cannot be withdrawn from the system. Q_2 molecules exhibit a certain zero-point energy in the gas phase. In metal hydride systems different potentials are present for the occupancy of an interstitial site either in an octahedral or a tetrahedral hole. In addition, these zero-point energies are dependent on the kind of bounded isotope.

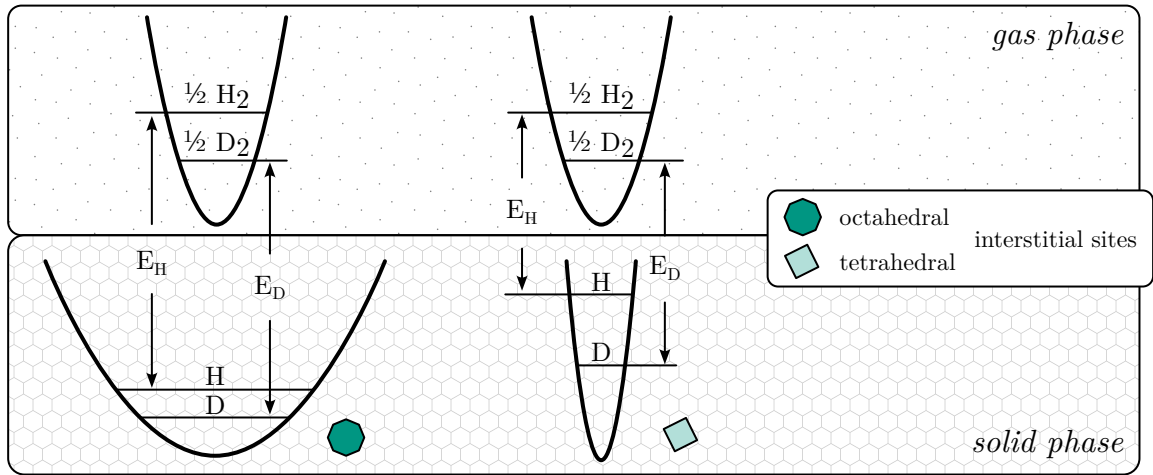


Figure 2.2: Schematic depiction of the zero-point vibrational energy levels of Q_2 molecules occurring in the gas phase and Q atoms in the interstitial sites of an octahedral and tetrahedral hole. [48]

The reduction of the energy potential due to metal hydride formation differs for the hole and isotope type. While the narrow and steep potential wall of a tetrahedral interstitial hole results in a larger energy gain for the absorption of heavier isotopes, the formation of light hydrides is accompanied by larger energy differences between the zero-point energy levels for an octahedral site. Which kind of interstitial side is present in the material is dependent on the metal lattice. Additionally, also two types of interstitial sites may occur within one material. [48, 38, 51]

The zero-point-energies $\hbar\omega_i$ can be calculated assuming an *Einstein oscillator*, revealing the following values for the isotope molecules: $\hbar\omega_{\text{H}} = 269$ meV, $\hbar\omega_{\text{D}} = \hbar\omega_{\text{H}}/\sqrt{2} = 190$ meV and $\hbar\omega_{\text{T}} = \hbar\omega_{\text{H}}/\sqrt{3} = 155$ meV [38, 50].

To express the distinction of the isotope effect of metal hydride formation, the separation factor α is used. It sets the abundance of the isotope species in the gas phase in relation to the composition of the solid phase of a binary isotope mixture according to

$$\alpha = \frac{z_{\text{light}}^{\text{G}}}{z_{\text{heavy}}^{\text{G}}} \left(\frac{z_{\text{light}}^{\text{S}}}{z_{\text{heavy}}^{\text{S}}} \right)^{-1}. \quad (2.5)$$

Here $z_{\text{light}}^{\text{G/S}}$ represents the molar fraction of the light isotope species in the gas (G) or solid (S) phase while $z_{\text{heavy}}^{\text{G/S}}$ equals the molar fraction of the heavy isotope species. The resulting value of α is a figure of merit which isotope effect is present.

$$\alpha \begin{cases} \ll 1 & \text{normal isotope effect} \\ = 1 & \text{no isotope effect} \\ \gg 1 & \text{inverse isotope effect} \end{cases} \quad (2.6)$$

In literature opposite definitions for *normal* and *inverse* isotope effect can be found. This controversy results from the different derivation of *normal*. Respecting the accelerating impact of the greater molar mass of heavy isotopes on the absorption kinetics, consequently it is more "normal" to react with heavy isotopes [38]. The other interpretation follows from the abundance of the respective isotope effects. Since most metals exhibit a preference to react with light isotopes, this is considered to be a *normal* isotope effect. Beside the distinction of *normal* and *inverse* the terms *positive* (normal) and *negative* (inverse) are common. In this work the term *normal* isotope effect expresses the tendency of an absorption material to react with light isotopes while materials showing an *inverse* isotope effect absorb preferably heavy isotopes of a mixture. [52, 49]

In addition, the isotope effect is dependent on the system temperature T due to the temperature dependence of the vibrational energies and the underlying equilibrium reaction of metal hydride formation. In general, increasing temperatures reduce the isotope effect. This can be expressed by the separation factor α , which according to [50] follows the logarithmic correlation

$$\ln(\alpha) = -\frac{A}{T} + B \quad (2.7)$$

where A and B are material dependent coefficients. For some materials the system temperature can decide whether a normal or inverse isotope effect is present [39].

To obtain the separation factor α of an absorption material, experimentally derived PCI can be utilized (c.f. Sec. 2.1.2). For an equal concentration c of isotope Q in the lattice and equal temperature, Eq. (2.5) simplifies to the ratio of the established equilibrium pressures, i.e.,

$$\alpha(c, T) = \frac{p_{\text{eq,light}}(c, T)}{p_{\text{eq,heavy}}(c, T)} . \quad (2.8)$$

This qualifies the measurement of isotope specific PCIs to be a versatile tool to identify the suitability of an absorption material for TSA technology.

2.2 Temperature Swing Absorption Process

A temperature swing absorption process for hydrogen isotope separation exploits the isotope dependent reaction during metal hydride formation. To apply this behavior within a separation process, an isotope distinguishing absorption material is filled into a column. When feeding a hydrogen isotope mixture into this packed column, the favored isotope species is absorbed preferably than the unfavored in the metal, and hence the unfavored species accumulates in the gas phase. This thermodynamic equilibrium driven separation equals a single separation stage. The achievable separation is defined by the separation factor α of the utilized material (c.f. Subsec. 2.1.3, Eq. (2.5)).

The overall separation is enhanced by establishing a flow of the isotope mixture through the packed column. This causes a chromatographic separation effect and introduces a multi-stage separation dependent on the column length and other parameters. [53] These described interactions are schematically shown in Figure 2.3. While the favored isotope species (smaller molecules in Fig. 2.3) is absorbed preferentially at the feeding point, the less favored isotope species (bigger molecules) travels further within the column and occupies remaining lattice places.

Additionally, isotopic exchange reactions occur, which are graphically represented by the reaction steps I, IIa and IIb. If the thermodynamic equilibrium has not established yet, the preferred isotope species may replace the already bounded less favored species. In step I the favored species dissociates at the metal surface and enters the metal lattice followed by step IIa which equals the release of the replaced unfavored species and their recombination. It should be highlighted, that during exchange reactions hetero-isotopologues may form (step IIb in Fig. 2.3), i.e., a molecule composed of a heavy and a light isotope. Due to these interactions, an isotope distribution, i.e., a concentration profile, results over the column length. The described physics represent a typical batch-type gas chromatographic separation process. To realize a quasi-continuous separation process exploiting chromatography, TSA processes couple two columns, between which an isotope mixture is periodically exchanged until the targeted concentration profile establishes and

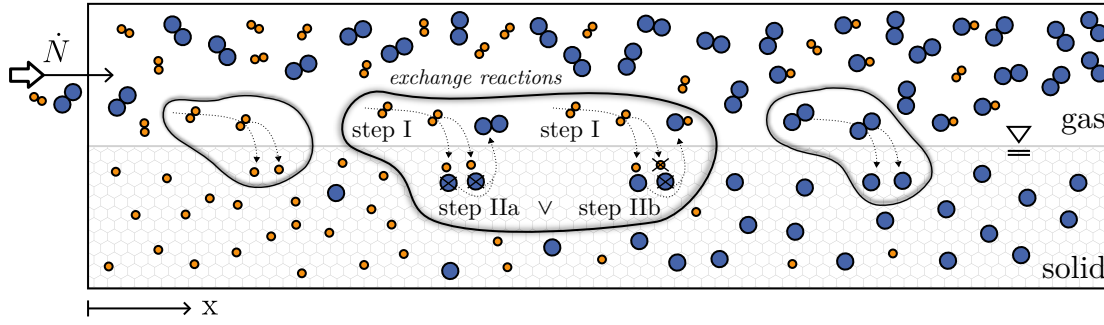


Figure 2.3: Schematic description of the gas chromatographic separation effect occurring in an absorbent when being flown through by a binary isotope mixture. The isotope species represented by small molecule sizes is favored and may replace already absorbed isotope species indicated by large molecule sizes when travelling through the column (isotope exchange reaction). The favored species dissociates at the material surface (step I) and replaces the less favored atom species, which recombines and emerges into the gas phase either as homo-isotopologue (step IIa) or hetero-isotopologue (step IIb).

product fractions of opposite isotope compositions are withdrawn. [34, 49, 54, 55, 56]

2.2.1 State-of-the-Art Thermal Cycling Absorption Process

A well known TSA process for hydrogen isotope separation is developed by Savannah River National Laboratories (SRNL) since the early seventies. The *Thermal Cycling Absorption Process* (TCAP) utilises palladium as active separation material which is deposited on either particulate alumina-oxide or particulate kieselguhr, serving as inert support material to optimize the gas-solid-contact and gas transport within the column. Additionally, the inert carrier serves for the mechanical stability of palladium during repeated hydrogenation and dehydrogenation. Palladium is a well-investigated absorption material, which preferably forms its light metal hydride, thus exhibits a normal isotope effect, detailed in Subsec. 2.3.2. To establish a gas flow through the selective Pd packing to promote a multi-stage separation as described above, in the TCAP the Pd column is coupled with a non-selective plug flow reverser (PFR) column (flow sheet shown in Fig. 2.4 a)). The PFR column is filled with an inert kieselguhr packing, which does not provide any separation efficiency and absorption capability. The gas exchange between both columns is temperature initiated and driven by the temperature swings of the Pd column, as detailed in the following. [34, 57, 58]

The TCAP processes a mixed isotope stream, which is transferred between the two columns several times. This is realized by cyclically changing the Pd column temperatures, which defines the pressure establishing within the column driven by the equilibrium of metal hydride formation. A heated Pd column in desorption phase is pressurized with the mixture of isotopes. When opening the separating valve V-exch between both columns, a pressure driven gas transfer to the PFR occurs. On the contrary, after clos-

ing the valve and bringing the Pd column into absorption phase by cooling, its resulting pressure is lower than the pressure in the PFR, such that the gas is transferred from the PFR to the Pd column when opening V-exch. Due to the isotope effect during palladium hydride formation, enhanced by the chromatographic effect as presented in Figure 2.3, a concentration profile across the Pd column establishes during processing. With each exchange cycle the isotope mixture is further separated. While a product fraction enriched in heavy isotopes can be extracted at the end of the Pd column (V-bottom, Fig. 2.4a)), at the head a product fraction enriched light isotopes accumulate (V-top, Fig. 2.4a)). After product withdrawal, which equals a small quantity of the total hydrogen inventory in the column, the extracted amount is topped up by re-feeding the mixed-isotope stream and the cycling is restarted. Therefore, a semi-continuous process operation results whose repeating process steps are summarized in Table 2.1. [34]

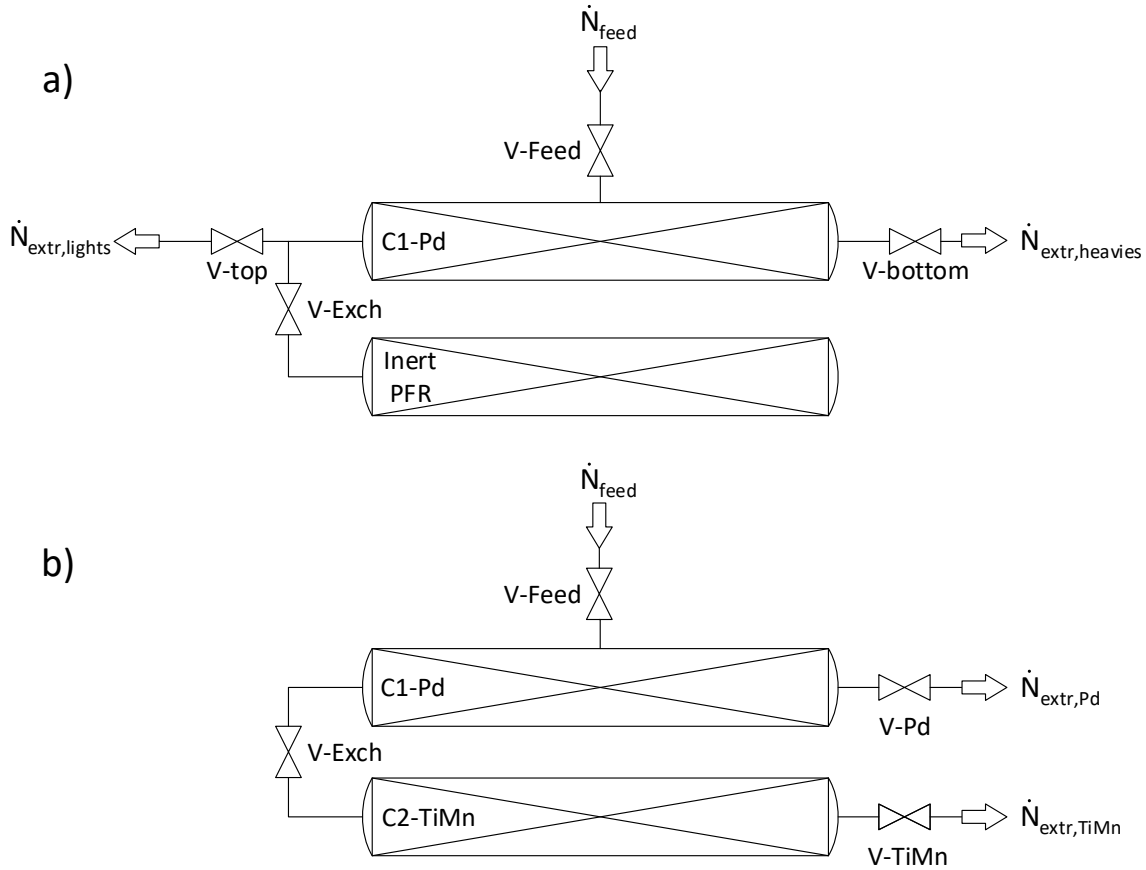


Figure 2.4: Flow sheets of the traditional TCAP using a PFR (a) and the CMH-TSA Process (b) with the corresponding feed valve V-Feed, exchange valve V-Exch and extraction valves V-top and V-bottom (TCAP) vs. V-Pd and V-TiMn (CMH-TSA). The selected labels for the CMH-TSA process are corresponding to the utilized absorbent material of the separation columns. The supply of feed stream and extraction of product streams occur during temporal different process steps (c.f. Fig. 2.5).

Even though TCAP has proven to be a versatile semi-continuous optimized chromatographic separation process, it does not fulfil all requirements for IRPR utility. First off all, to maximise the exchanged amount of gas as well as the separation efficiency of Pd, cryogenic temperatures (liquid Nitrogen) are used during absorption phase to provide a sufficient pressure difference between the Pd column and the PFR, since only the Pd packing provides an absorption capability and defines the pressure difference between both columns. Another reason for operating at 77 K is the temperature dependence of the separation factor which increases for lower temperatures (c.f. Subsec. 2.1.3 and Fig. 3.5). In addition, to support the transfer from the Pd bed to the PFR, a large PFR volume is necessary to allow for sufficient decomposition of the Pd hydride, as kieselguhr does not exhibit an absorption capability. Approximately one half of the Pd hydrogen storage capacity can be contained in the reported PFR design [54]. This means a large hydrogen amount remains in the Pd lattice and does not contribute to the separation, which can also be concluded from the reports of Heung et al. as the pressure measured in the PFR alternated between 1.7 to 2.8 bar, thus the Pd column pressure remained at 2.8 bar when transferring the gas phase to the PFR [35]. This leads to high tritium inventories and insufficient process throughput for IRPR application.

To enhance system throughput and separation efficiency, SRNL developed further TCAP concepts. Until now, different development stages of the process exist, focussing for example on more efficient heating systems, system sizes or Pd packings [59, 60, 61]. More advanced TCAP solutions replace the PFR by a selective molecular sieve. This has the advantage of having an opposite isotopic effect to palladium, thus actively contributing to the separation [35]. Instead of extracting both product fractions from the Pd column, a product stream enriched in light isotopes is sampled from the molecular sieve. However, to promote the separation effect of a molecular sieve by isotope dependent surficial adsorption, still cryogenic operational temperatures are mandatory [62, 63, 64, 35]. In fact, Heung et al. report temperature amplitudes of -196 to -100 °C between which the molecular sieve is alternated, causing a large energy demand. Although an increased product purification and doubled system throughput for this modification is observed, advanced TCAP solutions still suffer from scalability issues and high tritium inventories. Values stating the precise throughput of the TCAP are often classified [34] since TCAP is mainly applied for weapon use and is not optimized concerning the separation task within the fusion fuel cycle [60]. However, in a conceptual design report by Klein feed rates of 4 to 16 % of the total inventory are mentioned [54], while Heung et al. state a throughput of 4 standard litres per heating cycle for a molecular sieve TCAP configuration [35]. Estimating the cycle time to be 60 minutes by the scale of the given figures (Fig. 6 and Fig. 8 in [35]), a system throughput of $\sim 4.5 \cdot 10^{-5}$ mol/s results which equals 0.103 Pam³/s per

heating cycle. Assuming ideal separation efficiency, to process the minimal IRPR system flow of $11 \text{ Pam}^3/\text{s}$ (c.f. Sec. 1.2), ~ 108 parallel TCAP systems are necessary.

2.2.2 Introduction to CMH-TSA and Differentiation to TCAP

To overcome the throughput limitations, high tritium inventories and cryogenic operation of TCAP for the separation task required in the fusion fuel cycle, an optimized TSA process is being investigated at KIT [65, 26, 18]. The *coupled inverse and normal metal hydride reaction temperature swing absorption* (CMH-TSA) process sets itself apart from the TCAP by the introduction of a second selective packed column. This column is filled with a metallic absorption material, e.g., TiMn, that shows, like the molecular sieve, an opposite isotope effect to Pd during hydride formation. The advantage of a metal hydride forming material over the molecular sieve zeolite exhibits in the resulting process operation schedule and operational parameters, since the coupled metallic beds, e.g., Pd and TiMn, support each other during gas exchange, which is further detailed in Subsec. 2.2.3. The gas transfer between both is still realized by the anti-cyclic heating of both columns, which is typical for TSA processes. The obtained product streams are extracted at the column ends respectively (the corresponding process flow sheet of CMH-TSA is given in Fig. 2.4 b). In the following, the repeated CMH-TSA process steps are explained and set in contrast to the traditional TCAP using a PFR, while a summary is given in Table 2.1.

Step I

Column 1 (C1) is cooled and in absorption phase. In the column's mid a feed stream of mixed hydrogen isotopes is introduced. According to the equilibrium and the absorption kinetics the mixture is absorbed in C1. Meanwhile the second column (C2) is heated and in desorption phase. In the CMH-TSA process, a product fraction enriched in light isotopes is extracted from the columns end. In the corresponding TCAP scenario the inert PFR is at high pressure level.

Step II

The transfer valve V-exch between either PFR (TCAP) or C2 (CMH-TSA) is opened. Due to the pressure difference a gas flow from the PFR/C2 to C1 establishes and hydrogen absorbs in the metal lattice until the pressure between both columns equilibrates.

Step III

The column temperatures are switched. C1 is heated which results in isotope release from the metal lattice according to the equilibrium (desorption phase). Simultaneously, C2 is cooled (CMH-TSA) and the material absorbs remaining isotopes from the gas phase. The PFR is at its low pressure level.

Step IV

C1 reaches the desorption equilibrium pressure. In a TCAP scenario two product fractions are extracted from C1. While at the columns end a fraction enriched in heavy isotopes is extracted, at the opposite side of the column light isotopes accumulate. In contrast to that, in the corresponding CMH-TSA process only at C1s end a product stream with increased heavy isotope composition is extracted.

Step V

After product extraction is completed, the transfer valve between C1 and PFR/C2 is opened again, enabling a gas flow from C1 to the PFR/C2. TCAP: The PFR is now pressurized. CMH-TSA: Since C2 is cooled, absorption takes place according to the equilibrium.

Step VI

The column temperatures are switched. C1 is cooled and absorbs remaining isotopes in the gas phase. The PFR remains at high pressure level while in the CMH-TSA scenario isotopes emerge from the absorption material in C2 until the desorption pressure of the set-point temperature is reached.

Table 2.1: Repeated process steps within a cycle of the CMH-TSA process in comparison to TCAP. C1 refers to the absorption column filled with palladium, while C2 marks the absorption column filled with an absorption material showing an inverse isotope effect.

Process step	TCAP (c.f. Fig. 2.4a))	CMH-TSA (c.f. Fig. 2.4b))
I	Feed in cooled C1, PFR at high pressure level	Feed in cooled C1, Product extraction from C2 at V-TiMn
II	Gas transfer C2 $\rightarrow$ C1	Gas transfer C2 $\rightarrow$ C1
III	C1 heated, PFR at low pressure level	Temperature switch, C1 heated, C2 cooled
IV	Product extraction C1 from at V-top and V-bottom	Product extraction from C1 at V-Pd
V	Gas transfer C1 $\rightarrow$ C2	Gas transfer C1 $\rightarrow$ C2
VI	C1 cooled, PFR at high pressure level	Temperature switch, C1 cooled, C2 heated

The described process steps are repeated. The extracted amount of products is replaced by the feed stream. If only a small amount of the total columns inventory is withdrawn, the compositions of the enriched fractions re-establish within the described process steps. For higher product extraction amounts, so called closed cycles may become necessary.

This means instead of extracting products from the column(s) during each cycle, the processed feed mixture is transferred several times between the columns until the targeted product composition is reached. The more closed cycles are operated, the more distinct the separation, i.e., the enrichment at each columns end. This alternation of closed and open cycles consisting of individual process steps as described above is shown schematically in Figure 2.5 for the CMH-TSA process.

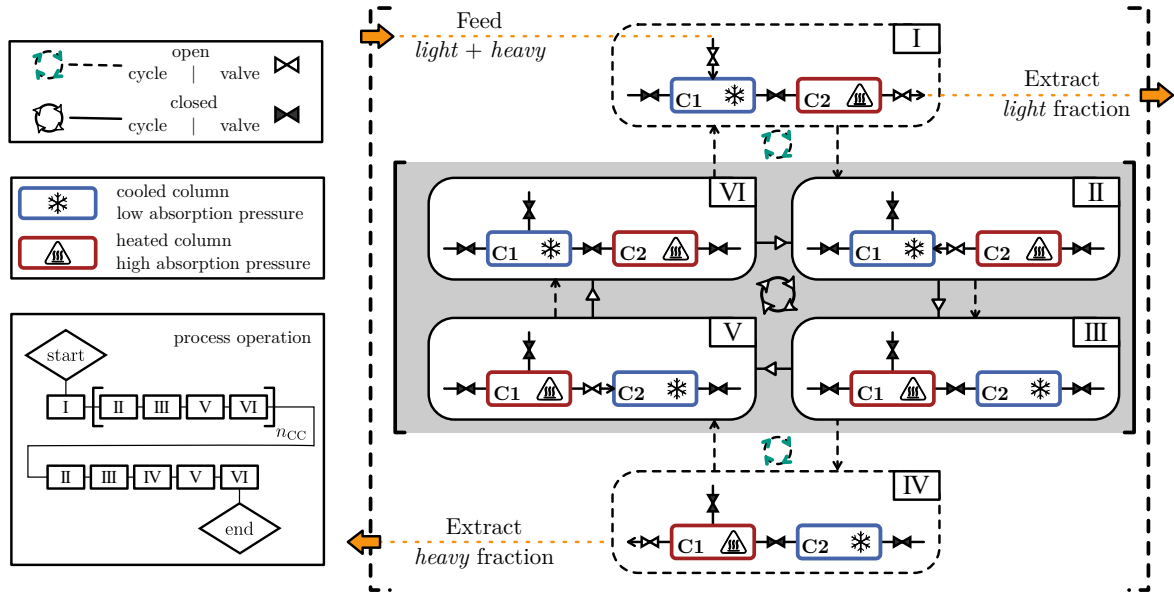


Figure 2.5: Schematic sequence of repeated process steps (I-VI) within a closed and open cycle loop of the CMH-TSA process presenting the corresponding valve position and column set-point temperatures at the different steps. Open cycles allow for matter transfer across the system boarder and are indicated by dashed lines. Closed cycles consist of process steps which realize gas exchange between both separation columns and are indicated by solid lines. Further details to each process steps are given in the text.

The thermodynamic phases both absorption materials pass in each process steps are presented in PCI diagram (c.f. Fig. 2.6). In this diagram the four process temperatures are shown, which allow for cycling a hydrogen isotope mixture between two absorption columns. The temperatures and materials are selected such that $p_{\text{eq},Q_2}(T_{\text{hot},C_2}) > p_{\text{eq},Q_2}(T_{\text{cold},C_1})$ and $p_{\text{eq},Q_2}(T_{\text{hot},C_1}) > p_{\text{eq},Q_2}(T_{\text{cold},C_2})$. Feeding Q_2 into the cooled C1 column results in increasing occupancy of hydrogen on the lattice, but the more significant increase is reached during gas exchange from C2 in C1 (II). In the same time, the concentration is lowered in I in C2 due to product extraction. In the exchange step, c decreases until pressure equilibration is reached between the columns. Now C1 has its maximum loading while C2 is at the lowest capacity operation point. The following temperature switch in III can be seen by a slight decrease in concentration for C1 while the column pressure significantly increases. On the other side C2 absorbs further hydrogen due to the lower equilibrium pressure present for the lowered temperature. While C2s state keeps

equal from III to IV, pressure and concentration in C1 is slightly reduced caused by the product extraction. In the following V the gas transfer between the columns again results in equal column pressures. This time the condition is the other way round, meaning C2 reaches its maximum loading while C1s inventory is at its lowest operation point. The switch in temperatures results in a pressure jump of C2 accompanied by a slight concentration reduction caused by reduced capacity at higher temperatures while the pressure in C1 decreases and the amount of hydrogen in the lattice increases. The schematic depiction shows the closed loop resulting from the process step combination. Matter exchange over the system boarder occurs during I and III.

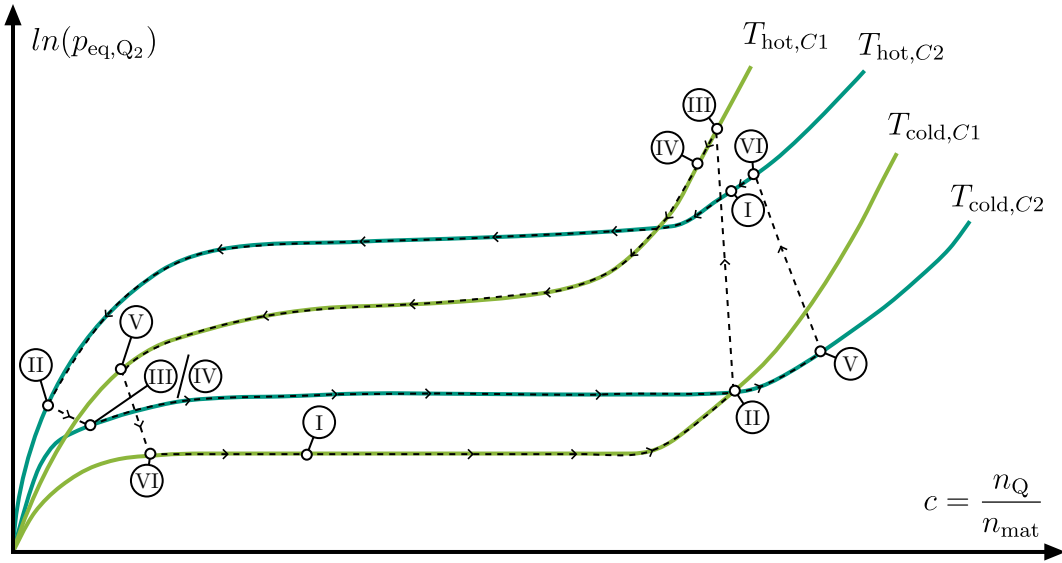


Figure 2.6: Thermodynamic phases of absorption materials when running through all CMH-TSA process steps (described in text).

2.2.3 Potential of the CMH-TSA Process

The presented CMH-TSA process operates two selective packed absorption columns, both exploiting a metal hydride forming bed, is able to enhance the process efficiency concerning the operation parameters, tritium inventory and obtainable enrichments. First of all, the separation performance of Pd is supported by the active separation capability of the partner material. Second, coupling two packed columns allows for operational process temperatures above -10°C , setting CMH-TSA apart from all TCAP solutions. While in the traditional TCAP using a PFR the gas exchange is driven by the operational temperatures of the Pd column, large temperature differences are required to provide a sufficient pressure delta between the columns. This means in order to minimize the non-exchanged hydrogen inventory which remains in the PFR, a very low absorption pressure has to be enforced, thus low temperatures are required. In turn, discharging the Pd column in

its desorption phase requires high temperatures, to release the absorbed hydrogen and to minimize the inventory in the Pd lattice. In advanced TCAP systems operating a molecular sieve, cryogenic temperatures are required to enable the surficial sieving effect. In contrast to the discussed TCAP solutions, CMH-TSA exploits the interaction of the coupled absorption materials, which support the discharge of the partner column respectively. Since emerging hydrogen is transferred from lattice to lattice, higher absorption and lower desorption temperatures can be used. As a side effect, pressure peaks are reduced and expansion volumes, i.e., the packing void fraction, can be minimized. Instead, it is necessary to adjust the material quantities of both columns such that comparable storage capacities are achieved.

Further advantages of the reduced temperature amplitude differences are the shortened necessary heating times. This not only significantly reduces energy consumption but also accelerates the integral process time and thus the time-averaged system throughput, which is assumed to overcome the scalability limitations of TCAP systems.

Finally, the mutual discharge of the combined column pair is expected to result in a significant reduction of the tritium inventory due to the minimized non-exchanged hydrogen loading in the columns during withdrawal.

Differentiation to coupled Palladium Beds

In literature the utilization of a second active separation column filled with an metallic absorption material has been realized by a second palladium column. This *simulated moving bed* (SMB) approach has been investigated experimental and theoretical by several researchers [66, 67, 68, 69, 70]. In general enhanced separation efficiency is reported and the potential of the process extension highlighted. Only Singh concluded that the utilized set-up is uneconomic for large technology scales as breakdowns during operation of the moving absorber bed occur [67]. The valve operation schedule of a SMB process is complex and in addition, up to five interacting palladium columns were used [66, 68]. Furthermore, the most recent publication of Robinson and Salloum who revived the approach of SMB using two columns was based on simulated approaches without experimental demonstration of capability [70]. Therefore, the development of an optimized TSA process, i.e., the CMH-TSA process, in this work is exclusively focussed on a second active absorption column filled with a material showing an inverse isotope effect. Utilising a second palladium column is not considered or investigated.

CMH-TSA Development: Status of Predecessor Work

This work builds on the predecessor work performed by Neugebauer, who, for the first time, considered extending the TCAP by using a second selective packed column with inverse isotope effect. To demonstrate the feasibility of this advanced process concept, a lab facility was planned and commissioned. The research additionally included the selection of a partner material showing an opposite isotopic effect to Pd. As a first approach, a titanium-chromium-alloy was investigated. The investigations were supported by the development of an equilibrium model. It was demonstrated, that in principle the separation of an isotope mixture is feasible using the CMH-TSA technology. Furthermore, parametric studies of process temperatures and cycle numbers on the separation efficiency were performed. However, the first material candidate $\text{TiCr}_{1.5}$ suffered from instabilities leading to non-reproducibility of experiments. Also, the first approach of an equilibrium model showed the versatility of the process, but revealed the necessity of a transient and dynamic model since kinetics have a non negligible impact on the estimated separation result. It should be mentioned that up to this point, the CMH-TSA process was supported by an upstream membrane which aimed for a rough pre-separation of the mixed isotope feed stream³. However, the TSA separation stage proved to be highly efficient to serve as stand-alone separation technology. Therefore, the pre-separation stage, i.e., the membrane, is not investigated further in this work. [65, 26]

This work focusses on the optimization of the utilized material couple, the in-depth process operation parameter investigation and optimization of the existing lab set-ups. The model is modified to enable one-dimensional transient and rigorous simulations of the process dynamics. Additionally, this allowed for implementation of the CMH-TSA model in the updated fuel cycle simulator developed by Schwenzer [22].

2.3 Materials for Temperature Swing Absorption

The separation efficiency, process temperatures and pressures, cycle times, etc. of the CMH-TSA process are highly dependent on the selected pair of materials. Not every hydride forming metal is suitable to serve for a TSA application. In this section, the requirements of a CMH-TSA material for the IRPR system in the EU-DEMO fuel cycle are defined and the selected candidates for experimental studies are presented.

³In fact, the early process development status was called *Membrane-Coupled Temperature Swing Absorption* process in order to highlight the combination of a membrane and a TSA separation stage.

2.3.1 Material Requirements for CMH-TSA

First of all, the absorption material has to exhibit a *distinct isotope effect*. Large separation factors reduce the necessary columns length and the number of required gas exchanges to reach the envisioned product enrichments. This in turn reduces the integral process time and thus the operable system throughput. Secondly, the values of the thermodynamic pressure-concentration-temperature characteristics have to be located within the envisioned operation range of the process. To be precise, a lower limit of $-10\text{ }^{\circ}\text{C}$ is envisioned, which enables the utilization of standard water-glycol cooling media. But also the *desorption temperatures* are limited to approximately $200\text{ }^{\circ}\text{C}$, as the energy consumption to realize the temperatures swings is directly linked to the delta of the temperature amplitudes. In addition, the times necessary for establishing the alternating temperatures increases for larger deltas and therefore impacts process time. For TSA applications so called *low temperature hydrogen storage metals or alloys* are of interest as those are characterized by providing desorption pressures of several bar at room temperature [39]. In fact, the *desorption pressures* should not exceed 2 to 4 bar, which allow system integration. On the other hand *absorption pressures* of a technical reasonable limit of several mbars are required as the lower the absorption pressure the higher the necessary temperature for desorption pressures in the targeted operation range. Since two absorption materials are combined in the CMH-TSA process, their characteristics have to be *adaptable* to each other thus pressure-concentration-temperature relations within the same order of magnitude. Otherwise this causes different material amounts, column geometries and operation parameters which lead to significant increase of process complexity. Beside the thermodynamic characteristics, the *kinetics of absorption and desorption* shall not limit the process cycling time, thus have to be faster than the heating and cooling kinetics. Materials with a reasonable *reversible hydrogen storage capacity* are required, as this reduces the material amount and increases the processable throughput while reducing residual hydrogen atoms in the metal lattice and therefore the tritium inventory. Since the materials are foreseen to absorb and release hydrogen isotopes in repeated cycles an important material feature is the *cycling stability*. Large numbers of tolerated cycles have to be enabled without tendency for decrepitation or decomposition, while showing reproducible characteristics without loss of capacity or drifts in the establishing equilibrium pressures. Finally, to limit risks for operators and environment, *hazard requirements* have to be respected which means materials are required that are non radioactive and exhibit *low pyrophoric, explosive and poisonous* characteristics. Thus the material handling has to be safe and controllable during operation, preparation and filling.

2.3.2 Pre-Selection of Material Candidates

A literature survey was performed to identify promising material candidates for CMH-TSA application. The challenge is to select two materials with opposite isotope affinity and matching sorption characteristics, which fulfil the requirements presented above. In addition, the isotope sensitivity is a rarely reported characteristic of metallic materials, as in general their absorption behavior is of more interest for hydrogen storage or thermochemical compression technology [41, 39, 71], whose functionality is not dependent on the isotope species. The non-existing necessity to differentiate between the isotopes for most technical hydrogen applications besides fusion technology causes a data gap of reported Metal-Q₂ interactions. Further on, studies concerning the separation, extraction and production of tritium are often classified, as they are of interest for defence and nuclear weapon technology. A detailed literature survey and review of promising absorption materials can be found in the predecessor work [26], as the identification of a first material pair was part of the TSA stage conceptualising. The following is a condensed survey summary, focussing on presenting the material candidates selected for the experimental studies performed in this work. A comparison between literature data and experimental results is given in Chapter 3 for each material candidate respectively.

Normal Isotope Effect

The most prominent material candidate showing a normal isotope effect is palladium. Its isotope dependent absorption characteristics are well reported in literature. Pd exhibits a very distinct isotope effect of and is therefore highly attractive concerning separation technologies [51, 72, 38, 73, 74]. Well-established separation technologies that utilize Pd are for example displacement chromatography or the TCAP (c.f. Sec. 2.2) [56, 75, 64, 76, 77]. Besides its catalytic effects used in various syntheses, it has the advantage of long-term cycling stability as the pure metal is not affected from disproportionation occurring in alloy compositions. Instead, Pd can be easily coated on inert supportive material which leads to enhanced gas-solid-contact during hydrogenation and reduced gas transport limitations.

However, the mayor drawback of Pd as separation material are its high costs. Therefore, attempts were made to find alternatives for Pd. Candidates were for example LaNi₅ or ZrCo [78, 79, 50]. However, in the investigated operation regime those materials are not as effective as Pd. Either disproportionation occurs or the separation effect is not distinct enough [80]. As the mayor selection criteria for this work on developing the CMH-TSA technology is the separation factor and the focus is on supporting the research hypothesis that a second material with inverse isotope effect intensifies the separation efficiency, Pd application is not questioned in this work.

Although, in comparison to other absorption materials, palladium is well explored concerning its isotopic preference of hydride formation, material characterization studies of the Pd sample used in this work for CMH-TSA are required. This is because the resulting absorption characteristics and, as a consequence, the separation factor are highly dependent on the palladium formulation, i.e., the type of carrier material used, the composite composition, the Pd particle size, etc. Albeit some absorption analyses of comparable Pd formulations are described in literature, most of these do not target the CMH-TSA temperature range of interest. In some cases, the analyses are even restricted to the separation factor of a particular test temperature, allowing only for identification of an isotopic preference. Consequently, reported absorption characteristics have to be extrapolated. Finally, the measured absorption data obtained within this work is serving as input data for the developed CMH-TSA model, which is presented in Chapter 5. Such required extensive data sets are not available in literature, especially for the various isotopologue species. A comprehensive discussion of the measured PCI and resulting separation factors of the Pd sample used in this work in comparison to literature values is provided in Subsection 3.2.1.

Inverse Isotope Effect

Identifying materials showing an inverse isotope effect is more challenging. The most valuable source of promising materials is the review of Andreev and Magomedbekov [50]. The researchers investigated several alloys towards their separation factor and isotope exchange reactions during their studies. However, this repository of isotopic preference of several metals and alloys summarizes either experimental separation factors for a specific temperature (varying for each material dependent on the references) or theoretical separation factors derived by simulation. Only for some materials the parameters A and B required for the temperature dependent separation factor correlation given in Eq. (2.7) are provided. Depending on the references, values for either α_{HD} or α_{HT} are given. This means, the review serves as valuable orientation to identify promising inverse candidates, but does not replace an experimental material characterization, due to the large data gaps.

Considering the targeted pressure and temperature range, especially Ti-alloys are promising for CMH-TSA application. These were investigated by Tanaka et al., giving a correlation between the separation factor and the valence electron to atom number ratio of the alloys [81]. From this the most distinct isotope effects are obtained for titanium-chromium alloys, followed by titanium-manganese alloys (Fig. 3 in [81]). The latter are especially of interest, as TiMn derivatives are known for being low temperature hydrogen storage materials. Nevertheless, TiCr-alloys were also taken into consideration and re-manufac-

tured, as they were the first choice in the demonstration campaign and a contamination incident was suspected to be the reason for unreproducible absorption characteristics [26, 65]. Furthermore, some researchers investigated the absorption and separation behaviour of TiCr-alloys of different compositions in *bcc* crystal formation, since *bcc* alloys are suspected to exhibit high storage capacities [82, 83]. The PCIs reported by Tamura et al. show promising absorption pressures and an inverse isotope effect for TiCr samples [84, 82, 83]. Since according to the researchers the composition, i.e., the proportion of Ti and Cr in the binary alloy, has an impact on the establishing absorption pressure, the composition was adapted such that the resulting absorption pressure is suitable for CMH-TSA operation (detailed in [26]). However, since it is not clear if this modification has an influence on the resulting separation factor, PCI measurements are required.

Concerning the isotope effect of TiMn alloys several studies are reported by Andreev et al. [85, 75]. These *Laves Phase* intermetallic compound forms hydrides in the promising operation range of CMH-TSA application and are therefore investigated as second material for the inverse candidate. However, as mentioned above, data towards the absorption behavior and thus separation factors of the binary TiMn_{1.5} alloy investigated by Andreev et al. do not cover the full CMH-TSA operation range of interest. The given *A* and *B* parameters are related to an experimental temperature range of 195 to 296 K, therefore the separation factor has to be extrapolated for higher temperature regimes (c.f. Fig. 3.10). In addition, in contrast to the binary TiMn_{1.5} sample, the analysed TiMn_{1.5} sample in this work is a multicomponent alloy. Further alloying components are used to lower the absorption pressure and to support cycling stability (c.f. Subsec. 3.2.4). Therefore, the resulting PCI have to be measured and, as explained above, it has to be verified, that the modification of the composition does not significantly impact or suppress the separation capability. Finally, as stated for the investigated Pd sample, the obtained absorption data is required for the CMH-TSA model, and is not available in literature in this detail degree.

Chapter 3

Material Characterization for Temperature Swing Absorption

To overcome the data gap in literature concerning isotope specific absorption behavior (c.f. Subsec. 2.3.2) and to obtain data sets to be implemented in the CMH-TSA model (c.f. Ch. 5), the set-up MAIA (*Material Investigation for Absorption*) is used to perform absorption studies and to characterize the material candidates selected in Subsec. 2.3.2. Furthermore, in this chapter hypothesis 3 is targeted, i.e., finding an absorption material showing an inverse isotope effect and PCI characteristics comparable to that of Pd. It should be highlighted, that for all experimental investigations and material characterizations only the hydrogen isotopes protium and deuterium were used. Tritium experiments require specialized laboratories and safety concepts due to tritiums radioactivity. Therefore, the isotope dependent absorption characteristics are derived by comparing protium and deuterium absorption data. To predict tritium absorption characteristics these results are extrapolated and simulations are performed. For this, the obtained protium and deuterium PCIs serve as input data for modelling the material characteristics required in the corresponding CMH-TSA model (c.f. Ch. 5). In the following, first the set-up MAIA is presented, followed by the description of the experimental procedure to measure PCIs. Then the manufacturing and preparation of the investigated materials are described and the obtained measurement results are discussed and compared to literature values concerning the separation factor and their utility for CMH-TSA application.

3.1 Experimental Set-up MAIA

The most common technique to measure PCIs is the *volumetric measurement method* which is performed in a so called *Sieverts' apparatus* [86]. By exposing an absorption material sample to a known hydrogen amount, the obtained pressure decrease allows for

calculation of the amount of absorbed hydrogen by using the ideal gas law. Repeated dosing of these hydrogen amounts enable the measurement of a completed PCI which covers all forming hydride phases. A process flow sheet of the utilized custom Sieverts' apparatus MAIA is given in Figure 3.1.

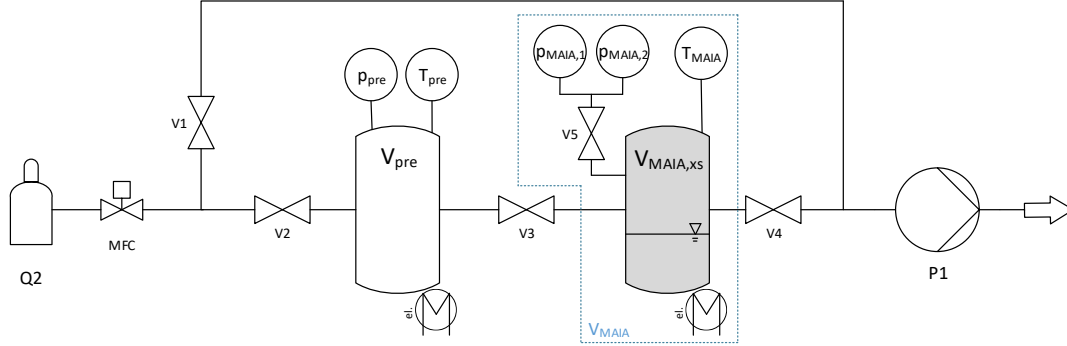


Figure 3.1: Flow sheet of the custom Sievert Apparatus' MAIA utilized for obtaining PCI data above room temperature. The dotted frame indicates the sample holder volume V_{MAIA} for experimental pressures below 4 bar. During operation above 4 bar valve V5 is closed, reducing the sample holder volume to $V_{MAIA,xs}$ which is represented by the vessel in grey scale. Further details to all set-up components are described in the text.

MAIA consists of two volume calibrated vessels: a pre-vessel (*Swagelok, 316L-HDF4-300*) for precise dosing of hydrogen amounts ($V_{pre} = 343.5 \pm 0.2$ mL) and a second vessel serving as sample holder ($V_{MAIA} = 88.3 \pm 0.4$ mL (empty)). Both vessels temperatures and pressures are measured using a sheath resistance thermometer T_{MAIA} (*TCdirect, Pt100 Type 18*, operation range -40 - 450 °C), a thermocouple T_{pre} (*TCdirect, Typ K*, operation range -100 - 400 °C) and gas independent capacity manometers covering different pressure ranges: p_{pre} and $p_{MAIA,1}$ (*MKS instruments, Baratron 627F14MBC1B*, max. pressure 10 bar) and $p_{MAIA,2}$ (*MKS instruments, Baratron 627F13MBC1B*, max. pressure 1 bar). In case of experimental pressures above 4 bar, valve V5 is automatically closed such that the capacity manometers are disconnected from the sample holder volume V_{MAIA} . This is necessary to protect the membrane in $p_{MAIA,2}$ from overpressure and thus prevent a sensor damage. During those pressure conditions p_{pre} is used for pressure record. The remaining sample holder volume $V_{MAIA,xs}$ measures 55.7 ± 0.2 mL (empty). The vessels temperatures are adjusted independently using heating cords (*TCdirect, HS/12*, max. 450 °C) and thermocouples (*TCdirect, Type K*). Since MAIA is only equipped with an electrical heating systems, the minimum experimental temperature for measuring PCIs is defined by the laboratory temperature, i.e., room temperature.

Either Argon, Deuterium or Protium can be dosed via a mass flow controller (MFC) (*MKS*

instruments, GE50A, operation range 2 to 100 sccm). For evacuating the system a turbo molecular pump P1 (*Edwards, TS85D1001*) is connected to the set-up. The pneumatic bellows valves (*Swagelok, SS-12BG-MM-5CM*) and heating systems are controlled via a humane machine interface (HMI) (*Siemens, WinCC*).

3.1.1 Calibration of Volumes and Temperature

For precise measurement of a PCI the determination of the gas volume of each vessel V_{MAIA} , $V_{\text{MAIA,xs}}$ and V_{pre} is necessary. Therefore, volume calibrations were performed for each investigated sample. First, a gas sample cylinder volume was calibrated (*Swagelok, 316L-HDF4-1000*) using distilled water. Thus the calibration volume was filled several times with water and weighed. The volume of 1045.6 ± 1.3 mL follows from the environment temperature, the measured weight using a calibrated scale and tabulated water density values. This calibrated volume was then used to determine the set-up volumes by using the Boyle-Mariotte approach. To do so, argon was fed in the calibration vessel while measuring the temperature and the pressure. By expanding the gas consecutively into V_{pre} , $V_{\text{MAIA,xs}}$ and V_{MAIA} , the volume follows from the pressure equilibration and the ideal gas law. For each material sample V_{MAIA} and $V_{\text{MAIA,xs}}$ have to be recalibrated because of the volume taken up by the metal.

To calculate c for each dosing step, beside accurate gas volumes, the precise gas temperature is required. Since temperature sensitive components of MAIA, like the capacity manometers and valve seats, are not insulated¹, temperature distributions occur. These lead to deviations between the measured material temperature and the gas temperature during a sorption experiment, which has to be corrected. Non uniformity of temperature within Sieverts' apparatus is a common phenomenon and unavoidable. Also commercial devices use routines to calibrate vessel volumes, gas temperatures, etc. before measuring PCIs to reduce systematic errors [86, 89]. For MAIA temperature correction, an effective gas temperature T_{eff} is determined which equals the mean gas temperature in the vessel. The same approach was used by Lässer et al. during their PCI determination of several Q₂-Me systems [90]. To obtain T_{eff} of all contributing vessels and vessel combinations either temperature ramps or the Boyle-Mariottes-Approach at relevant temperatures were utilized. By using the ideal gas law, T_{eff} is calculated from the pressure present at room temperature $p(T_{\text{RT}})$ and the pressure establishing for the elevated temperature $p(T_{\text{eff}})$

¹The utilized capacity manometers have an upper temperature limit of 45 °C for their housing to protect electrical parts [87]. In addition, valve seats are not insulated as they should not be operated above 150 °C according to manufacturers declaration and to maintain disassembly capability [88]. However, especially during bake-outs, higher temperatures need to be operated. Since capacity manometers show a high measurement accuracy and are independent from the measured gas species, they are highly preferred for the PCI determination. Therefore, the necessity of temperature calibration is accepted.

according to

$$T_{\text{eff}} = \frac{p(T_{\text{eff}})}{p(T_{\text{RT}})} \cdot T_{\text{RT}} . \quad (3.1)$$

This temperature calibration reveals linear correlations between T_{eff} and the set-point temperature T_{set} for each volume constitution occurring during a sorption experiment. As can be seen in Figure 3.2, the discrepancy between these temperatures is maximised for V_{MAIA} as at this vessel both temperature sensitive and therefore non-insulated pressure sensors $p_{\text{MAIA},1}$ and $p_{\text{MAIA},2}$ are connected and T_{eff} decreases with the proportion of uninsulated contributing components. For example, $T_{\text{eff}}(V_{\text{MAIA}})$ is almost 100 °C lower than $T_{\text{set}} = 150$ °C. As this is a difference of 66.7 %, the impact on the calculation of c is not negligible.

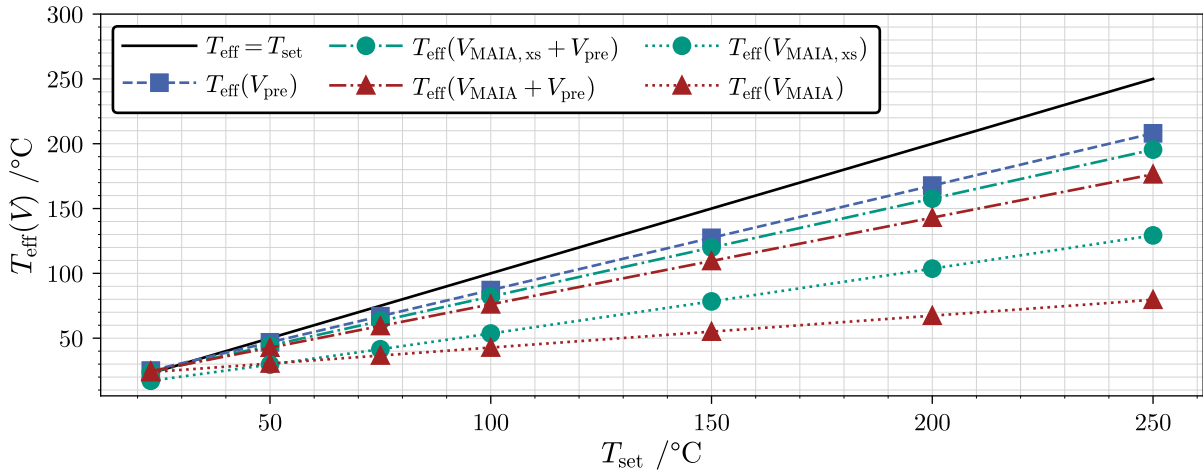


Figure 3.2: Correlation of establishing effective gas temperatures for each vessel and vessel combination utilized during a MAIA sorption experiment with respect to the set-point temperature. Error bars are smaller than the markers.

3.1.2 Procedure of MAIA Experiments

To determine the separation factor and absorption characteristics, PCI were measured using either protium (H_2 , purity = 99.9999 %) or deuterium (purity = 99.9 %) for different temperatures (room temperature = ~ 23.5 °C, 50 °C, 75 °C, 100 °C, 150 °C and 200 °C) depending on the material sample. The complete PCI is measured by given stepwise hydrogen portions to the absorption material, whereby the next portion is dosed after the pressure reaches equilibrium.

First the pre-vessel is filled with hydrogen using the mass flow controller. The amount of hydrogen supplied is then calculated from the pre-vessel volume V_{pre} , the effective gas temperature $T_{\text{eff,pre}}$ of the pre-vessel and the pressure p_{pre} using the ideal gas law (first term in the bracket in Equation (3.2) and (3.4)). Then the connecting valve (V_3 , c.f. Fig. 3.1) between both vessels is opened and hydrogen absorbs in the material driven

by the thermodynamic equilibrium of the hydride formation reaction (Eq. (2.1)). After reaching the equilibrium, i.e., no further pressure decrease greater than the pressure sensor accuracy is measured, the amount of absorbed hydrogen n_Q and the resulting load of atomic hydrogen absorbed in the lattice c for the dosing step i is calculated by

$$c_0 = \frac{2 \widetilde{M}_{\text{mat}}}{R m_{\text{mat}}} \cdot \frac{\Delta n_Q}{n_{\text{mat}}} = \frac{2 \widetilde{M}_{\text{mat}}}{R m_{\text{mat}}} \cdot \left(\frac{V_{\text{pre}} \cdot p_{\text{pre}}(\text{V3 closed})}{T_{\text{eff}}(V_{\text{pre}})} - \frac{(V_{\text{pre}} + V_{\text{MAIA}}) \cdot p_{\text{MAIA}}(\text{V3 open})}{T_{\text{eff}}(V_{\text{pre}} + V_{\text{MAIA}})} \right) \quad (3.2)$$

and

$$c_i = c_{i-1} + \frac{\Delta n_Q}{n_{\text{mat}}} = c_{i-1} + \left\{ \begin{array}{l} \frac{2 \widetilde{M}_{\text{mat}}}{R m_{\text{mat}}} \cdot \left(\underbrace{\frac{V_{\text{pre}} \cdot p_{\text{pre}}(\text{V3 closed})}{T_{\text{eff}}(V_{\text{pre}})} \Big|_i}_{\text{Dosed } n_{Q_2} \text{ in } V_{\text{pre}}} + \underbrace{\frac{V_{\text{MAIA}} \cdot p_{\text{MAIA}}}{T_{\text{eff}}(V_{\text{MAIA}})} \Big|_{i-1}}_{n_{Q_2} \text{ in } V_{\text{MAIA}} \text{ from step } i-1} - \underbrace{\frac{(V_{\text{pre}} + V_{\text{MAIA}}) \cdot p_{\text{MAIA}}(\text{V3 open})}{T_{\text{eff}}(V_{\text{pre}} + V_{\text{MAIA}})} \Big|_i}_{\text{Not absorbed } n_{Q_2} \text{ in } V_{\text{MAIA}}} \right), \quad p < 4 \text{ bar} , \\ \frac{2 \widetilde{M}_{\text{mat}}}{R m_{\text{mat}}} \cdot \left(\underbrace{\frac{V_{\text{pre}} \cdot p_{\text{pre}}(\text{V3 closed})}{T_{\text{eff}}(V_{\text{pre}})} \Big|_i}_{\text{Dosed } n_{Q_2} \text{ in } V_{\text{pre}}} + \underbrace{\frac{V_{\text{MAIA, xs}} \cdot p_{\text{pre}}}{T_{\text{eff}}(V_{\text{MAIA, xs}})} \Big|_{i-1}}_{n_{Q_2} \text{ in } V_{\text{MAIA, xs}} \text{ from step } i-1} - \underbrace{\frac{(V_{\text{pre}} + V_{\text{MAIA, xs}}) \cdot p_{\text{pre}}(\text{V3 open})}{T_{\text{eff}}(V_{\text{pre}} + V_{\text{MAIA, xs}})} \Big|_i}_{\text{Not absorbed } n_{Q_2} \text{ in } V_{\text{MAIA, xs}}} \right), \quad p > 4 \text{ bar} , \end{array} \right. \quad (3.4)$$

where $\widetilde{M}_{\text{mat}}$ is the molar mass and m_{mat} the mass of the investigated material sample. Factor 2 results from dissociation of molecular hydrogen in the gas phase to atomic hydrogen in the lattice. The second term in the bracket in Equation (3.4) refers to the amount of Q_2 in V_{MAIA} (or $V_{\text{MAIA, xs}}$ for $p > 4$ bar) which remained in the gas phase during the previous dosing step $i - 1$. In Equation (3.2), i.e., for the first dosing step $i = 0$ this mid term is obsolete, as the sample holder volume V_{MAIA} is evacuated before opening valve V3. The last term represents the amount of non-absorbed Q_2 in step i after pressure equilibration between V_{pre} and V_{MAIA} (or $V_{\text{MAIA, xs}}$) and established absorption equilibrium.

These steps are repeated until a complete PCI is obtained or the absorption pressure out-ranges the operation limit of MAIA (> 10 bar). A schematic absorption pressure development over the experimental time and the resulting PCI is shown in Figure 3.3.

After the experiment the vessels are pumped down using the turbo molecular pump P1 and the material is baked-out at around 320°C for 12 hours to release residual hydrogen from the lattice for the next PCI determination which is verified by falling below the measurement range of $p_{\text{MAIA},1}$ ($< 10^{-2}$ mbar). The underlying uncertainty determination for the obtained concentrations are given in detail in the appendix, following a Type B uncertainty estimation (c.f. Subsec. B.1.1, [91]) while the uncertainties of the utilized sensors are given in Table B.1.

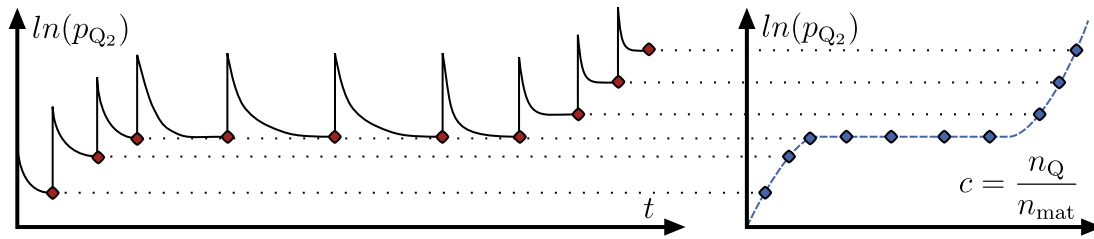


Figure 3.3: Schematic depiction of obtained absorption pressures over time during a typical MAIA experiment (left) and the resulting pressure-concentration-isotherm (right).

3.2 Characteristics of Material Candidates

In the following the analysed absorption materials and their observed characteristics are presented, including the specific manufacturing process and the activation routine. To evaluate the utility as TSA material candidate, PCI results and the derived metrics like the separation factors or the van't Hoff parameters are discussed and set into context with reported literature data. All investigated Ti-alloys were manufactured by *Fraunhofer Institute for Applied Materials (IFAM) Dresden*. In the following, whenever data is presented referring to the commercial Sieverts' apparatus *KEP Setaram*, *GasPro HA* or the magnetic suspension balance *Rubotherm*, *Isosorp 2* measurements were performed by IFAM within the scope of a respective material development contract work. For some material investigations PCIs out-ranged the operational range of MAIA, for example if pressures outreached 10 bar and temperatures lower than room temperatures were of interest. If the commercial Sieverts' apparatus or MAIA were utilized is pointed out at the respective data discussion. All described manufacturing procedures and activation treatments are based on manufacturers experience and advice.

3.2.1 Palladium Characteristics

Although Pd is a well explored isotope distinguishing absorption material, a sample was investigated in this work. The reason for this is the PCI dependence on the specific Pd formulation, i.e., the composite composition of Pd and an auxiliary material (see below). In addition, the obtained data serves as input for the PCI model implemented in the developed CMH-TSA model (c.f. Subsec. 5.2.1). As in the predecessors work [26] desorption pressures of the utilized Pd composite were measured, the repetition to identify absorption isotherms for this work was unavoidable. Finally, the comparison of obtained Pd PCI data and literature allows for validating the measurement accuracy of the set-up MAIA.

Palladium Sample

Palladium coated on inert γ -Al₂O₃ spheres of 0.8 mm in diameter was used for this work. The composite was prepared by *Fa. Chemical Consulting Dornseiffer (Jülich)* using an impregnation process. The resulting weight percent of active Pd is 30 %, while the bulk density of the packing is 1.2 g/mL. The diameter of the spheres is adapted to the column geometry of HESTIA (c.f. Subsec. 4.1.1) such that wall influences on the gas flow can be neglected, hence $d_p/D_{col} < 0.1$ is valid. The utilization of support material enhances the gas-solid-contact during the metal hydride reaction and suppresses transport limitations, i.e., reduces the pressure drop over the columns length. In addition, the stress on the structural material caused by the metal lattice expansion during hydride formation is reduced.

Activation

To enable hydrogen absorption, Pd has to be activated first since it reacts to palladium oxide in air atmosphere. Therefore, the sample was heated up to 200 °C and kept in a hydrogen flow of 20 sccm at 1 bar for approximately 2 h. Then the hydrogen atmosphere was hold for another 2 h at 200 °C and 1 bar. During this treatment PdO reacts with H₂ and forms water according to the equilibrium reaction



PdO does not absorb H₂ and inhibits the PdH formation. The completed activation treatment was verified by testing the absorption capacity at room temperature and compare it to literature values.

PCI Results

$8.4 \text{ g} \pm 8.4 \cdot 10^{-5} \text{ g}$ Pd-Al₂O₃ composite ($n_{\text{Pd}} = 0.024 \text{ mol}$) were investigated in MAIA and PCIs were determined at room temperature, 50 °C, 100 °C, 150 °C and 200 °C with H₂, D₂. The resulting absorption isotherms are shown in Figure 3.4. The characteristic phases (α , $\alpha - \beta$ and β) are clearly distinguishable from each other. While the pure α -phase is observable for c up to 0.1 mol_Q/mol_{Pd}, the pure β -phase establishes for $c > 0.65 \text{ mol}_Q/\text{mol}_{\text{Pd}}$. A moderate Plateau-Sloping is observed, which increases with temperature. Further on, for increasing temperatures the transition from plateau-region to β -phase shifts to lower c , thus reduced hydrogen capacities. In addition, temperature increase is accompanied by increasing equilibrium pressures for both investigated isotope species as expected.

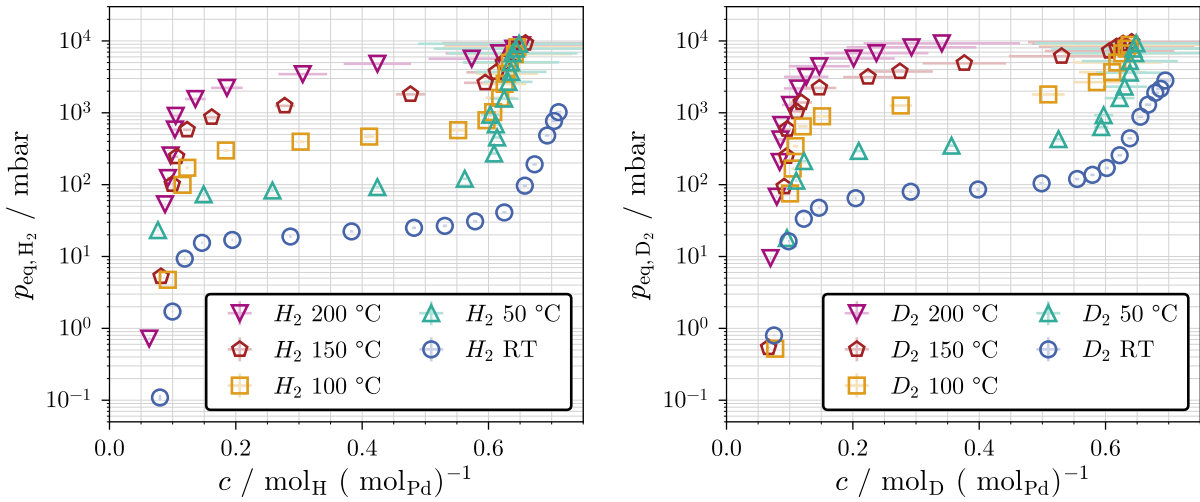


Figure 3.4: Establishing absorption equilibrium pressures for various temperatures in dependence of the absorbed Q amount and isotope species in the Pd lattice. Left: H₂ exposure, right: D₂ exposure. Error bars calculated according Type B uncertainty estimation using sensor uncertainties (c.f. Tab. B.1).

Comparing the resulting pressures in regard of the utilized isotope species, for each investigated temperature the establishing equilibrium pressure of the Pd-H₂-system is lower than the corresponding equilibrium pressure of the Pd-D₂-system for similar c . This is the consequence of the normal isotope effect, thus the favored Pd protide formation, which is also reflected in greater capacities for the H₂ storage at equal temperatures.

The obtained room temperature plateau pressures are $\sim 20 \text{ mbar}$ (H₂) and $\sim 80 \text{ mbar}$ (D₂) and increase to approximately 1100 mbar (H₂) and 1400 mbar (D₂) at 150 °C. The corresponding separation factor α_{HD} can be calculated according to Eq. (2.8) for equal c . The temperature dependence is shown in Figure 3.5 in comparison to separation factors reported by Wicke and Nernst [73] and Sharpe et al. [72] according to Eq. (2.7).

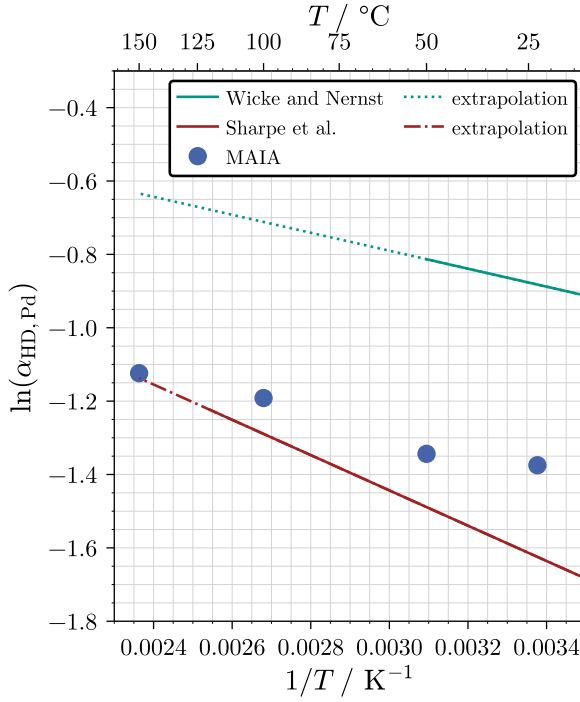


Figure 3.5: Temperature dependence of the separation factor α_{HD} for palladium as obtained from MAIA investigations and reported values derived by parameters A and B (Eq. (2.7)) [73, 72]. Doted lines represent extrapolations of the reported temperature range. Error bars are smaller than the symbols.

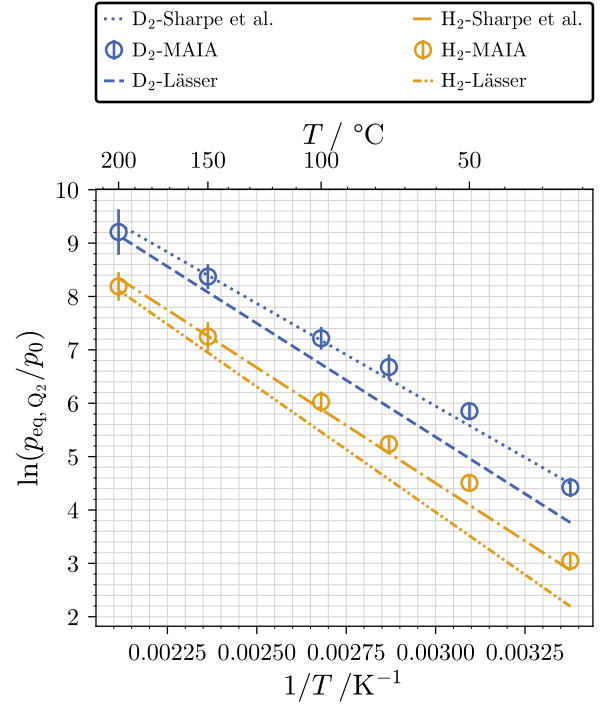


Figure 3.6: Van't Hoff plots of the analysed palladium in MAIA compared to van't Hoff parameters reported in literature [72, 51] in the investigated temperature range (293 to 473 K) for protium and deuterium. For $T < 50^\circ\text{C}$ the error bars are smaller than the symbols. p_0 refers to the standard pressure of 1000 mbar.

The most distinct separation factor α_{HD} of 0.25 occurs at room temperature, reducing to 0.33 at 150°C . The correlation proposed by Wicke and Nernst reveals a value of $\alpha_{\text{HD}} = 0.41$ at room temperature while Sharpe et al. report $\alpha_{\text{HD}} = 0.2$. The large deviations are related to the different Pd systems investigated. Wicke and Nernst analysed the absorption behavior of a palladium black foil while Sharpe et al. analysed a Pd getter bed of $d_p = 44 - 149 \mu\text{m}$, thus a higher specific surface. The Pd formulation in the getter bed is more comparable to the Pd formulation of the here utilized Pd- Al_2O_3 composites, therefore the measured separation factors are in line with the results reported by Sharpe et al. The lower separation efficiency obtained by Wicke and Nernst for a Pd black foil might be related to the lower specific surface or transport limitations within the foil.

To compare the observed equilibrium pressures with literature reporting of the Pd- Q_2 systems, a van't Hoff diagram is given in Figure 3.6 while the corresponding van't Hoff parameters identified for Pd- Al_2O_3 are listed in Table 3.1. Sharpe et al. measured absorption isotherms similar to this work, whereas Lässer performed desorption measurements [72, 51]. Therefore, all system temperatures reveal remarkably lower equilibrium pressures for investigations of Lässer in comparison to data obtained from MAIA experiments

which is related to the gas hysteresis (c.f. Subsec. 2.1.2). In addition, the formulation of the investigated Pd sample of Lässer, a Pd rod of 1.2 mm in diameter, differs to the Pd-Al₂O₃ composite of this work. In contrast, the measured absorption pressures for the comparable Pd getter bed sample reported by Sharpe et al. are again in line with MAIA results. This observation not only verifies the measurement accuracy of MAIA, but also proves the inert behavior of Al₂O₃ towards hydride formation as the absorption characteristics of particulate Pd are not affected.

3.2.2 TiCr_{1.2} and TiCr_{1.5} Characteristics

A TiCr-alloy was selected as first material candidate showing an inverse isotope effect for the demonstration of the TSA concept [65]. However, during the first HESTIA campaign, the utilized TiCr_{1.5} did not show the expected separation performance [26]. It was assumed, that poisoning or contamination did occur. According to the separation factors reported for Ti-alloys (c.f. Subsec. 2.3.2, [81]), TiCr-alloys exhibit the most distinct isotope effect and are therefore of high interest for TSA utility. Hence, it was decided to re-manufacture a TiCr-alloy sample, thus two TiCr absorption material samples were ordered from IFAM.

Shirasaki et al. correlated the composition of TiCr to the establishing absorption pressure [84], allowing for the determination of two promising compositions: TiCr_{1.5} as it promises the highest separation factor according to Tanaka et al. and TiCr_{1.2} as it provides a more adaptable absorption pressure range to Pd. However, the composition adaption may impact the separation efficiency. For both TiCr samples no support material like in the case of Pd was utilized, as the identification of a suitable material showing an inverse isotope effect has been the main focus of the material characterization studies, while future technical formulation is of interest after suitability demonstration. This decision was intended to limit potential error sources, like for example incidental interaction of the carrier material with hydrogen, which may distort interpretation of absorption characteristics. Furthermore, IFAMs manufacturing experience concerning metal hydride composites especially covers carbon support materials. Regarding the fusion fuel cycle, carbon utilization is seen critical, since carbon materials bear the risk to form tritiated hydrocarbons. Unfortunately, during separation experiments in HESTIA it turned out, that a support material is essential to provide sufficient mechanical stability and distribution of the packing within the absorption columns (c.f. Sec. 4.5).

TiCr_{1.2} and TiCr_{1.5} Samples

Titanium cylinders and chromium-granulates (both from *HMW Hauner*) were alloyed via arc melting in argon atmosphere at 0.7 bar. A heat treatment at 1370 °C for 24 h at 1 bar argon pressure was performed to reduce lattice tension. After this, the temperature was lowered to room temperature using a cooling rate of 20 K/min. The targeted compositions of the TiCr_{1.2} and TiCr_{1.5} granulates were verified using a SEM-EDX analysis (c.f. Tab. A.1, Fig. A.3 and A.4, appendix).

Activation

According to manufacturers recommendation a sample treatment at 300 °C in a 10 bar hydrogen atmosphere for 1 h followed by 30 minutes of evacuation repeated for three times is necessary. This enables the removal of the passivating oxide layer on the sample surface. Afterwards, the sample was flushed for 1 h using H₂ at 1.5 bar, followed by pressure cycling treatment at room temperature between 1.5 and 120 bar (H₂) for 20 cycles in total using a magnetic suspension balance (*Rubotherm, Isosorp 2*) to evaluate the reversible absorption capacity and to trigger decrepitation of the TiCr granulates to fine powder of final equilibrium size which equals usually 5 to 15 µm². Furthermore, during this cycling, residual α -titan irreversible hydrides to titan hydride.

PCI Results

During the first MAIA experiments it became obvious that no complete PCI, i.e., the determination of all phases, is obtainable in this set-up, as the establishing equilibrium pressures exceed the maximum operational pressure already in the α -phase. Therefore, the commercial Sieverts' apparatus *KEP Setaram, GasPro HA* at IFAM was used for PCI measurements of both TiCr compositions, since it allows for operation in high hydrogen pressure regions up to 200 bar. Automatisations of this commercial Sievert's apparatus allows for quick measurements, therefore each PCI was measured 4 times each in contrast to measurements performed in the MAIA set-up. The resulting PCIs are shown in Figure 3.7 using H₂.

In contrast to the PCI data discussed for the Pd sample, the PCIs obtained for both TiCr alloy samples exhibit a distinct sloping, such that the existence of a plateau can be ques-

²The final equilibrium particle size was not measured. Instead, reaching the equilibrium particle size is verified, as soon as no further capacity change during cycling in the magnetic suspension balance is observed. The required number of absorption cycles is performed in the Sieverts' apparatus before PCI determination accordingly.

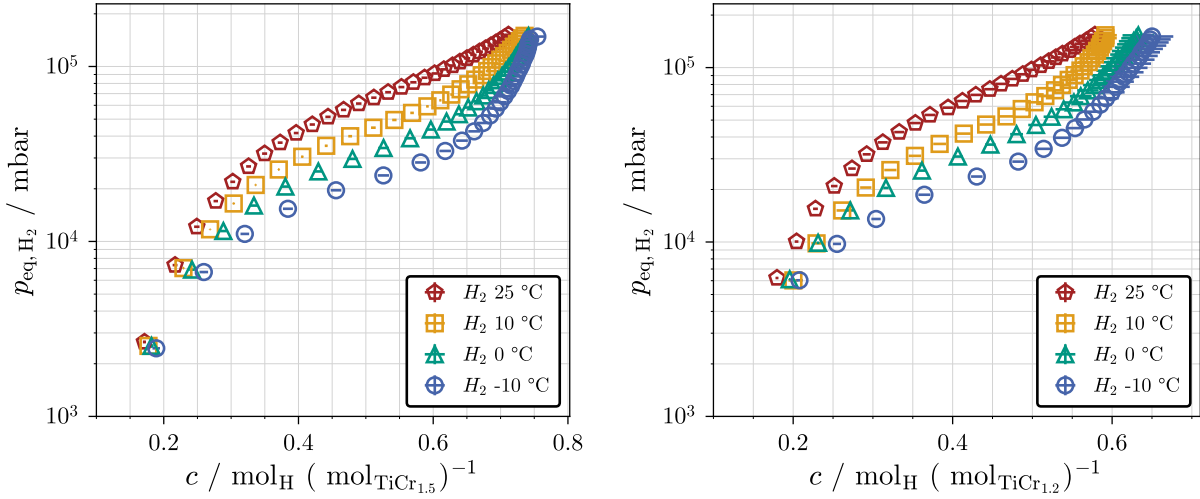


Figure 3.7: Measured absorption pressure-concentration-isotherms for $\text{TiCr}_{1.5}$ (left) and $\text{TiCr}_{1.2}$ (right) using H_2 at different temperatures. Error bars represent standard deviation of three repetitions.

tioned. However, comparing the shape of the PCIs to the data reported by Johnson for $\text{TiCr}_{1.9}$ protide formation, this sloping appears common for TiCr materials [92]. To differ between the phase regions introduced in Subsec. 2.1.2 the following definitions are used. The α -region is defined between the concentration range $c = 0$ to $c = 0.25$. The upper concentration value is related to the first inflection point of the PCI. The $\alpha - \beta$ -region spreads between $c = 0.25$ to $c = 0.7$ ($\text{TiCr}_{1.5}$) and 0.55 ($\text{TiCr}_{1.2}$), i.e., the second inflection point. From the data follows that even for the lowest tolerable process temperature of -10°C equilibrium pressures outreaches 10 bar for concentrations of $c = 0.15$ in the α -phase. The sloping plateau pressure exhibits values from 10 to 30 bar, while the β -phase reveals even pressures up to 100 bar. The van't Hoff parameters are derived by the pressures in the mid of the $\alpha - \beta$ -region of each sample and are listed in Table 3.1.

Surprisingly, the adapted composition does not affect or rather lower the plateau pressure as assumed from the reported results from Tamura et al. [82, 83]. However, the difference in alloy composition clearly results in a capacity adjustment. While $\text{TiCr}_{1.5}$ reveals a hydrogen capacity of up to $0.76 \text{ mol}_\text{H} / \text{mol}_{\text{TiCr}_{1.5}}$ at -10°C the lower chromium portion in the $\text{TiCr}_{1.2}$ sample results in a reduced capacity of $0.66 \text{ mol}_\text{H} / \text{mol}_{\text{TiCr}_{1.2}}$. While the TiCr PCI data reported by Tamura et al. and Shirasaki et al. differ from the obtained pressures of this study [82, 83, 84], Johnson, who investigated the metal-hydride formation of $\text{TiCr}_{1.9}$, observed related pressure characteristics [92]. To understand this discrepancy, the Ti-Cr phase diagram has to be consulted (c.f. Fig. A.1 in the appendix).

Both chosen TiCr compositions are located within the two phase region of α -Ti and TiCr_2 . The adaption of the Ti:Cr ratio impacts the proportion of those phases (c.f. Tab. A.2).

While α -Ti stores hydrogen at low equilibrium pressures and is classified as no reversible hydrogen storage material since high desorption temperatures for hydrogen release are required, TiCr_2 exhibits the observed equilibrium pressures. The presence of two-phases explains the similar equilibrium pressures, which are related to the TiCr_2 -phase while the capacity is affected by the differing composition. To understand the contrary results of the reported equilibrium pressures by [82, 83, 84, 92], the crystal lattice is taken into consideration. $\text{TiCr}_{1.2}$ and $\text{TiCr}_{1.5}$ alloys manufactured in this work consist of *Laves*-phases (c.f. Fig. A.2, appendix) while Tamura et al. and Shirasaki et al. froze the melted alloy into a metastable *bcc* lattice since those are suspected to exhibit higher hydrogen storage capacities. As for TSA an absorption material is required, which provides outstanding long-term cycling stability, a metastable alloy lattice is not considered to inherit this property. The missing plateau-region of the $\text{TiCr}_{1.5}$ investigations performed by Neugebauer during previous works are related to this conclusion. The TiCr samples were not poisoned, instead the α -region was investigated and exploited during HESTIA and MAIA experiments. Nevertheless, the inverse isotope effect was identified by the results, being in accordance with the investigations of [81].

3.2.3 $\text{TiMn}_{1.5}$ Alloy Hydralloy C5 Characteristics

The second Ti-alloy group having a distinct inverse isotope effect according to investigations by Tanaka et al. [81] are TiMn alloys, which are known for being so called low temperature hydrogen storage materials (c.f. Subsec. 2.3.2). Also Andreev and Magomedbekov observed the affinity for absorbing heavy isotopes of $\text{TiMn}_{1.5}$ during their studies towards isotope sensitivity of hydride forming intermetallic composites [85, 50].

The most common representative of TiMn alloys are the commercial alloy group called *Hydralloys* which are developed for hydrogen storage techniques applied automotive and submarine technology [93, 39]. These alloys show excellent long-term cycling stability and fast absorption kinetics. A well explored candidate of this group is *Hydralloy C5* (C5) which PCI characteristics are close to required CMH-TSA operation range. However, since C5 is a multicomponent TiMn -based alloy, first it has to be evaluated if the separation factor is affected by the other alloying elements.

Hydralloy C5 Sample

The investigated material sample of *Hydralloy C5* (GfE Metalle und Materialien GmbH) is a single phase alloy which consists of *C14-Laves* crystal structures. Its composition is $\text{Ti}_{1.01}\text{Zr}_{0.08}\text{Mn}_{1.48}\text{Fe}_{0.10}\text{V}_{0.42}$ and the formulation form are granulates which pulverize during hydrogenation to equilibrium particle size. As discussed for the TiCr samples, no support material was used.

Activation

The C5 sample was activated similar to the procedure described for TiCr (c.f. Subsec. 3.2.2). A hydrogen atmosphere of 10 bar was kept for 6 h at 300 °C, then the sample was charged at room temperature up to 30 bar with hydrogen for 4 cycles to trigger de-crepitation.

PCI Results

The PCIs were measured by IFAM using the high pressure Sieverts' apparatus *KEP Setaram, GasPro HA* to obtain a complete isotherm within the temperature range of interest. From literature reports the plateau pressure at room temperature of C5 is close to 10 bar and therefore at the maximum operation range of MAIA. Since temperatures lower than room temperature cannot be operated in MAIA, again the commercial Sieverts' apparatus was used. The resulting PCI for H₂ and D₂ at -10, 0 and 20 °C are shown in Figure 3.8.

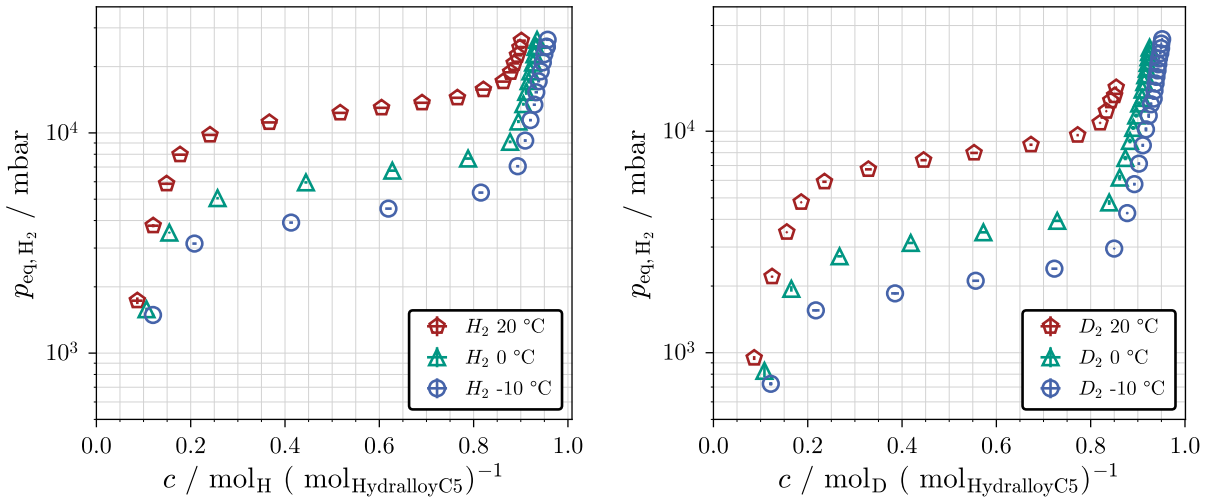


Figure 3.8: Measured pressure-concentration-isotherms of the TiMn_{1.5} alloy "Hydralloy C5" using H₂ (left) and D₂ (right). Error bars represent standard deviation of three repetitions.

At room temperature a slightly sloping plateau pressure of 10 to 15 bar establishes for protium while 4 to 5 bars are observed at -10 °C. Indeed, the inverse isotope effect is present, as comparison with the deuterium exposure data reveals: For 20 °C, 6 to 10 bar are measured which lower down to 1 to 2 bar for -10 °C. A calculation of the separation factor reveals 2.0 (-10 °C), 1.85 (0 °C) and 1.6 (20 °C). These α_{HD} resemble those reported by Andreev and Magomedbekov who measured $\alpha_{HD}(228 \text{ K}) = 1.6$ [50] showing that even though C5 is a multicomponent alloy, it seems not to affect the isotope effect which TiMn_{1.5} exhibits. Furthermore it results that the hydrogen storage capacity of C5

is comparable to Pd showing an $\alpha - \beta$ -phase transition at $c = 0.8 \text{ mol}_\text{H}/\text{mol}_{\text{C5}}$.

Another benefit of the single phase C5 is the possibility to tune the equilibrium pressure by adapting the proportion of the partner alloying elements. In particular zirconium has the functionality to reduce the equilibrium pressure [94, 95, 96]. Therefore, a second TiMn alloy was manufactured, targeting lower equilibrium pressures while keeping the separation factor unaffected.

3.2.4 Modified TiMn_{1.5,mod} Alloy Characteristics

TiMn_{1.5,mod} Sample

To lower the equilibrium pressure further to reach more comparable absorption characteristics as Pd, a TiMn_{1.5} alloy derivate of C5 was manufactured that has the same composition as C5 except for an increased proportion of zirconium. The technical melting of precise pre-calculated compositions is challenging, as during arc melting alloying components tend to evaporate. The resulting composition of the adapted alloy is therefore slightly deviating from the targeted composition. SEM-EDX measurements revealed a final alloy constitution of $\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.48}\text{Fe}_{0.10}\text{V}_{0.42}$ after arc melting and heat treatment (c.f. Tab. A.3). An examination of the present phase structure revealed one phase *C14-Laves* structures as C5 (c.f. Fig. A.5).

Activation

First, the same activation procedure as applied for Hydralloy C5 was performed to break oxide layers and trigger decrepitation (c.f. Subsec. 3.2.3). However, cycling the sample in an H_2 atmosphere using the magnetic suspension balance lead to a reduction in capacity for each hydrogenation cycle. This phenomenon appears if degradation of a multicomponent storage materials occur [44, 39]. In a second attempt the strategy of activation was switched. This time, the sample was kept in a 5 bar H_2 atmosphere for 24 h (this pressure is above the plateau pressure at this temperature). Also Andreev et al. reported the spontaneous absorption capability of TiMn_{1.5} alloys during their investigations [85]. Afterwards, repeated hydrogenation of the sample showed stable loading and de-loading cycles and a reversible capacity (c.f. Fig. A.7). Nevertheless, as soon as the first hydride formation is completed, a contact with oxygen has to be strictly avoided otherwise irreversible contamination and passivation occur.

PCI Results

After completed activation, the $\text{TiMn}_{1.5,\text{mod}}$ sample was evaluated towards its isotope effect by measuring PCIs for $-10, 0, 20, 30$ and $40\text{ }^{\circ}\text{C}$ using H_2 and D_2 . Again, for this analysis the commercial Sieverts' Apparatus *KEP Setaram GasPro HA* at IFAM was used, to ensure measurements of full range PCIs and to enable similar temperature conditions, i.e., $T < \text{room temperature}$, as for the C5 sample. The results are shown in Figure 3.9. Comparing the establishing equilibrium pressures still the inverse isotope effect reveals, as H_2 isotherms exhibit higher absorption pressures than corresponding D_2 isotherms for equal c . But more important is the significant reduction of the absorption pressures such that for $20\text{ }^{\circ}\text{C}$ a plateau pressure from 500 to 1100 mbar is obtained for H_2 and 300 to 760 mbar for D_2 .

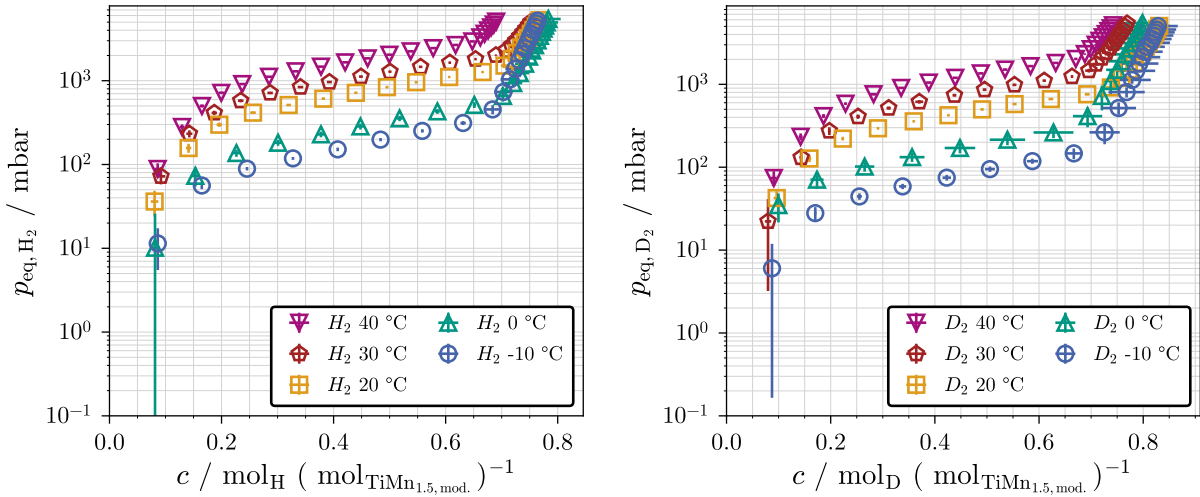


Figure 3.9: Pressure-concentration-isotherms of the modified TiMn-alloy at various temperatures for H_2 (left) and D_2 (right). Error bars represent standard deviation of three repetitions.

Being successful in reducing the room temperature absorption pressure to be lower than 1 bar, a second modification of the alloy composition was done. As Pd shows a plateau pressure of 20 mbar at $20\text{ }^{\circ}\text{C}$, this modification shall give an idea of minimal reachable pressure limit. To do so, the vanadium proportion was tuned as a further increase of Zr reduces the desorption kinetics and alloy stability towards degradation [96]. The final composition after melting and heat treatment was obtained from SEM-EDX measurements to be $\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.38}\text{Fe}_{0.10}\text{V}_{0.52}$ (see Tab. A.3 for targeted values and Fig. A.6 for phase investigation). Cycling was performed following the same activation procedure as used for the first modified composition. Here, a loss in capacity was clearly observed (c.f. Fig. A.8), supporting the assumption of degradation. In addition, it was remarkable that especially the desorption kinetic in the α -phase was more reduced than for the other

investigated TiMn candidates. Furthermore, a reduced capacity is observed. As the second modification suffered from severe stability issues, it was not investigated further.

From the described PCI characteristics the separation factor of the modified $\text{TiMn}_{1.5,\text{mod}}$ alloy is derived as well as the van't Hoff parameters. The latter are given in Table 3.1. In Figure 3.10 the temperature dependence of α_{HD} obtained from the establishing plateau pressures in the plateaus mid are given for the original C5 and the modified TiMn composition ($\text{TiMn}_{1.5,\text{mod}}$) in comparison to data measured by Andreev and Magodbekov. It should be mentioned that the parameters for Eq. (2.7) reported by [50] are obtained for a temperature region of 195 to 296 K. Thus the values for $\ln(\alpha_{\text{HD}})$ are extrapolated for elevated temperatures.

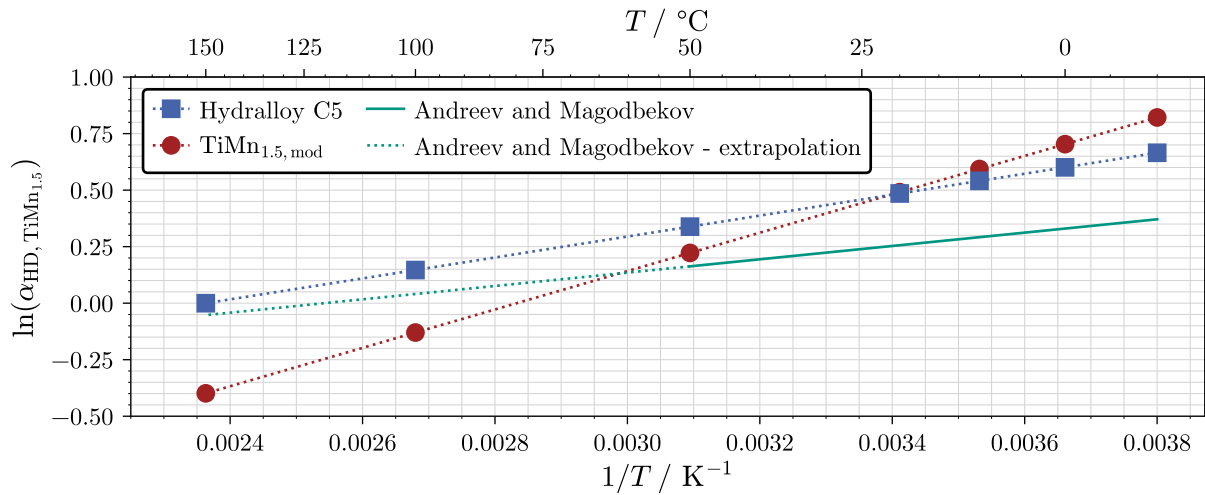


Figure 3.10: Temperature dependence of the separation factor α_{HD} for Hydralloy C5 and $\text{TiMn}_{1.5,\text{mod}}$ as obtained from PCI measurements compared to literature correlation according Eq. (2.7) reported by [50]. Error bars are smaller than the markers.

Comparing the obtained separation factors reveals that for $T < 50^\circ\text{C}$, $\alpha_{\text{HD,C5}}$ and $\alpha_{\text{HD,TiMn}_{1.5,\text{mod}}}$ are greater than those reported by [50] for binary $\text{TiMn}_{1.5}$. This may be caused by the other components. However, this observation switches for $T > 50^\circ\text{C}$, then the separation factors of C5 and binary $\text{TiMn}_{1.5}$ are almost identical, while $\alpha_{\text{HD,TiMn}_{1.5,\text{mod}}}$ is significantly reduced. For -10°C , i.e., the lowest investigated temperature in CMH-TSA operation range, the highest α_{HD} are observed: 2.3 ($\text{TiMn}_{1.5,\text{mod}}$), 1.9 (C5) and 1.45 (binary $\text{TiMn}_{1.5}$ [50]).

Interestingly, a critical temperature exists, where the inverse isotope effect switches to a normal one. This is the case at 150°C for C5 ($p_{\text{eq,H}_2} = p_{\text{eq,D}_2} = 233 \text{ bar}$) and at 80°C for $\text{TiMn}_{1.5,\text{mod}}$ ($p_{\text{eq,H}_2} = p_{\text{eq,D}_2} = 6.2 \text{ bar}$). Applying the same approach to the palladium system delivers a critical temperature of 293°C resulting in an equilibrium plateau pressure of 156.7 bar. However, a critical pressure of $p_c = 20 \text{ atm}$ is reported for this temperature, meaning the two phase regime vanishes at this temperature [97]. Thus, at this point no

isotope separation factor is defined, meaning that in the full palladium-hydride-formation range a normal isotope effect is present and explains the almost ideal parallel van't Hoff straights of Pd for H₂ and D₂ in Figure 3.11.

Table 3.1: Summarized isotope dependent van't Hoff parameters (absorption) of investigated absorption materials according Equation (2.4) ($p_0 = 1000$ mbar).

Material	Isotope	ΔH [kJ/mol]	ΔS [kJ/molK]
TiCr _{1.2}	H ₂	-21.93±0.83	0.1054±2.985 · 10 ⁻³
TiCr _{1.5}	H ₂	-20.75±0.36	0.1009±1.303 · 10 ⁻³
<i>Hydralloy C5</i>	H ₂	-23.17±0.19	0.0999±0.677 · 10 ⁻³
	D ₂	-27.02±0.34	0.1090±1.243 · 10 ⁻³
TiMn _{1.5,mod}	H ₂	-32.15±1.41	0.1082±5.115 · 10 ⁻³
	D ₂	-39.21±0.54	0.1282±1.876 · 10 ⁻³
Pd-Al ₂ O ₃	H ₂	-33.20±0.94	0.139±4.229 · 10 ⁻³
	D ₂	-30.60±1.43	0.142±5.907 · 10 ⁻³

3.3 Conclusions of Material Investigations

Several promising material candidates were investigated towards their absorption characteristics and isotope effect of hydride formation. A van't Hoff plot of the obtained temperature and isotope dependent equilibrium absorption pressures of all candidates is shown in Figure 3.11. In there, also the operation range for the CMH-TSA process used as technology for the IRPR system of EU-DEMO is given. Pd exhibits a normal isotope effect and benchmarks the targeted PCI characteristics of suitable hydride formation for being exploited in the CMH-TSA process. As partner material to be paired with Pd in this process, four Ti-alloy compositions were investigated. Since TiCr alloys show absorption pressures out of the targeted range, they are excluded from being used in the separation process. Instead, low temperature TiMn_{1.5} alloys derivatives are suitable candidates. They were not only shown to exhibit an inverse isotope effect, but also PCI characteristics in the same order of magnitude as Pd. To further adapt the establishing equilibrium pressures of the commercial hydrogen storage TiMn_{1.5} multicomponent alloy *Hydralloy C5* to those of Pd, its composition was modified in its Zr content. This lead to plateau pressures below 1 bar at room temperature. Thus, research hypothesis 3 is strengthened as a material is identified, showing an inverse isotope effect and being combined with Pd in the CMH-TSA process.

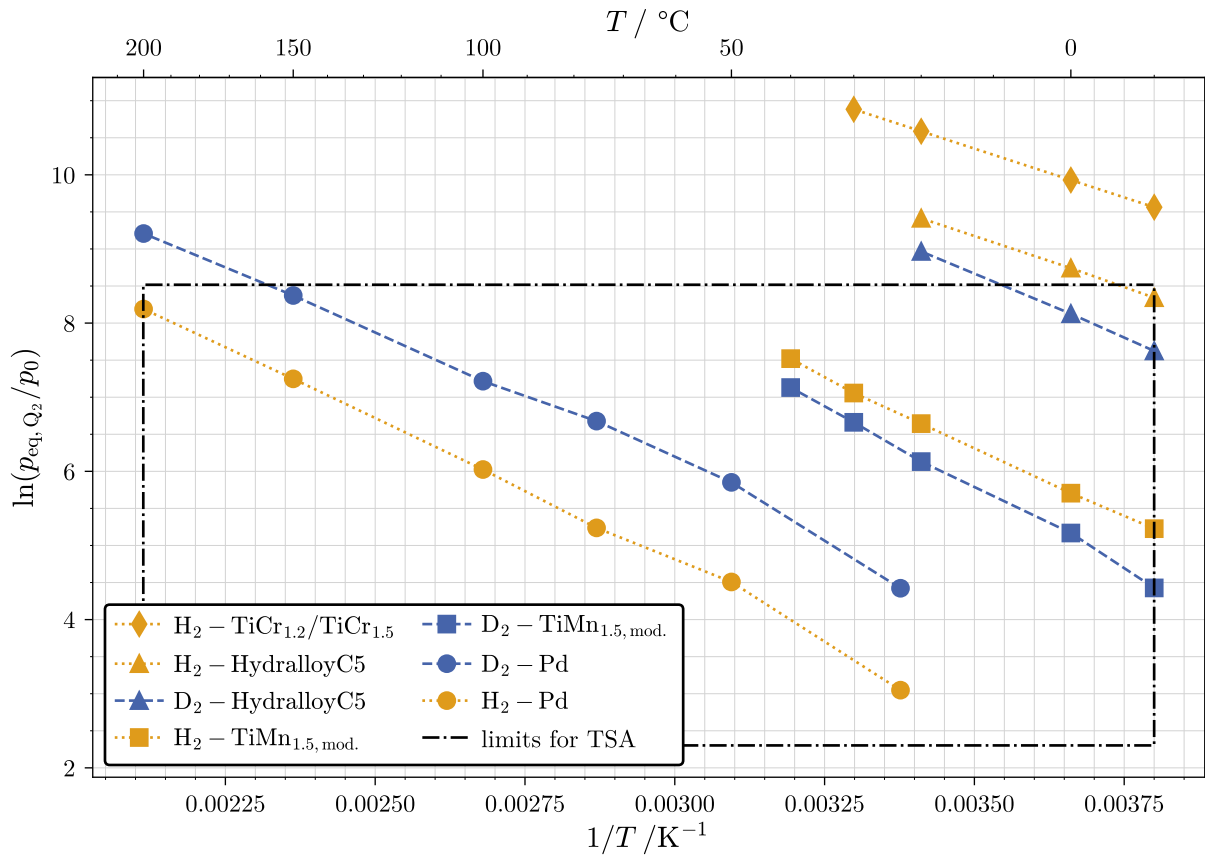


Figure 3.11: Van't Hoff plot of investigated absorption materials correlating the plateau pressure to the inverse system temperature for H_2 and D_2 exposure. Error bars are smaller than the symbols. Dashed lines refer to the operation range targeted for the CMH-TSA process envisioned for EU-DEMO IRPR.

However, the obtained separation factor of this modified $\text{TiMn}_{1.5,\text{mod}}$ alloy is lower than the separation factor of Pd, which can be concluded from the reduced gap between the isotope dependent van't Hoff straights and Figure 3.12 which summarizes the observed separation factors α_{HD} of all investigated absorption materials. Respecting the temperature dependence of α_{HD} , it was identified that the inverse isotope effect of the modified $\text{TiMn}_{1.5,\text{mod}}$ alloy hydride reaction disappears for $T > 80^\circ\text{C}$. This is a further restriction for the operation parameters for the CMH-TSA process developed in this work. As the establishing equilibrium pressure for this temperature is above 5 bar, this finding does not limit the utility of the identified material. Nevertheless, further research in material investigation are advised. Additional tests in adapting the composition have the potential to further optimize materials concerning their isotope effect of hydride formation while enhancing the stability and PCI characteristics, which is out of scope of this work. This also includes optimization concerning the formulation of $\text{TiMn}_{1.5,\text{mod}}$, i.e., the deposition on a suitable carrier material comparable to the $\text{Pd-Al}_2\text{O}_3$ sample. Using a $\text{TiMn}_{1.5,\text{mod}}$ composite supports mechanical stability and even distribution within the separation column.

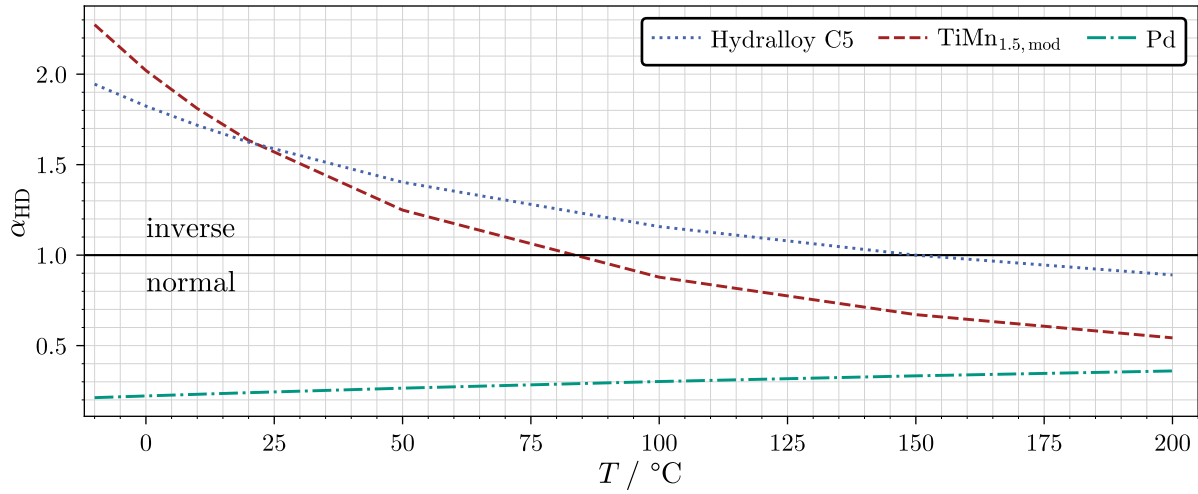


Figure 3.12: Temperature dependent separation factor α_{HD} for analysed materials in the operational temperature range of CMH-TSA. Data obtained by van't Hoff parameters presented in Table 3.1.

Therefore, as suitable material combination to be tested in separation experiments, Pd and TiMn_{1.5,mod} are selected. In addition, the measured PCI characteristics serve as input data for the CMH-TSA process model described in detail in Chapter 5.

Chapter 4

Isotope Separation Experiments

The selected material pair, i.e., Pd-Al₂O₃ and TiMn_{1.5,mod}, identified in Chapter 3 is used to perform separation experiments in the laboratory set-up *Hydrogen Experiments for Separation with Temperature Initiated Absorption* (HESTIA), which was assembled during the predecessors work [65, 26]. HESTIA is a test facility, which enables CHM-TSA and TCAP experiments on laboratory scale using non-tritiated hydrogen species only¹. HESTIA operation explores the separation efficiency of a single column and of coupled columns, allowing for evaluation whether coupled metal hydride reaction beds enhance the achievable separation efficiency of a single Pd column (hypothesis 2). Further on, parametric studies concerning the variation of operational parameters, e.g., the temperatures amplitudes, the number of cycles, the amount of processed hydrogen and its composition, can be analyzed towards the impact on product compositions. In addition, HESTIA is designed to allow for various interconnections and gas exchange routes, such that the identification of the most efficient process operation is possible. Finally, the obtained results shall verify the assumptions towards the advantages of CMH-TSA operation (c.f. Subsec. 2.2.3) and serve for validation of the developed CMH-TSA model presented in Chapter 5.

Unfortunately, the first experiments showed that the TiMn_{1.5,mod} packing did not provide the expected absorption and separation behavior as obtained during the presented material studies. Therefore, this chapter serves to present the diagnose and identification of error sources. Those investigations revealed that the functionality of the TiMn column is irreparable within the scope of this work. However, as detailed in Section 5.3, the data of the performed (diagnose) experiments and Pd column operations enabled the validation of the developed CMH-TSA model. The verification of hypothesis 2 will be addressed by

¹As described in Chapter 3 tritium experiments require specialised laboratories and safety precautions due to tritiums radioactivity. Therefore, the separation efficiency of a CMH-TSA experiment is evaluated by the separation of H₂ and D₂ mixtures.

means of simulations using this validated CMH-TSA model.

First, the adapted set-up and analytics are introduced and the activation of each material packing is described. Afterwards, results of different investigated operation modes are presented, like single column separation evaluation of each absorption column and separation tests using both columns. Based on the diagnose experiments, suggestions are given for further optimization potential of future CMH-TSA set-ups and material formulation.

4.1 Experimental Set-up HESTIA

Components installed in HESTIA can be categorized in several sub systems which are described in the following. A flow sheet of the main components is shown in Figure 4.2 while the complete P&ID flow sheet is given in the appendix (c.f. Fig. B.2 to B.5). Figure 4.1 shows a photograph of HESTIA and a CAD drawing of an installed column surrounded by a milled duroplastic plate used for heating (c.f. Subsec. 4.1.2).

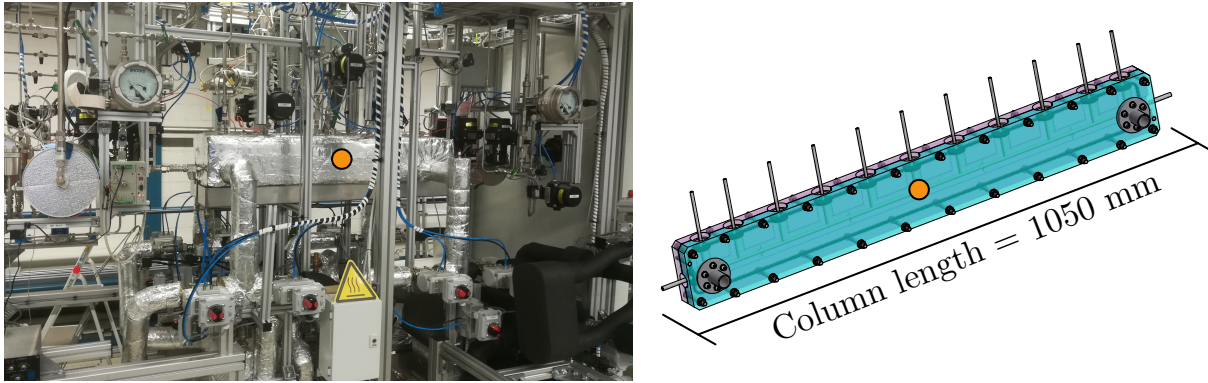


Figure 4.1: Left: Photograph of the laboratory set-up HESTIA. Right/orange circular marker: CAD drawing of an installed absorption column and mounted duroplastic plate serving as heat exchanger. Further details of all set-up components are described in the text.

4.1.1 Absorption Columns

The core of the experimental set-up are two absorption columns manufactured from *Swagelok* pipes of 316L vacuum steel having an inner diameter of 6 mm and 1050 mm in length (C1 and C2). Connectors of *Swagelok* pipes of 4 mm in inner diameter are welded at this main pipe to enable sensor connection. At each column two capacity manometers (*MKS instruments*, *Baratron 627F13MBC1B*, *627F14MBC1B*, maximum pressure p1/p3: 1000 mbar and p2/p4: 10 000 mbar) are installed, to enable gas species independent absolute pressure measurement. The temperatures are obtained using multiple Pt100 sheath resistance thermocouple (T1, T2, T3 and T4) (*TCdirect*, *Pt100 Type 18*, operation range -40 - 450 °C). For safety reasons, a burst disk of 30 bar opening pressure is installed at

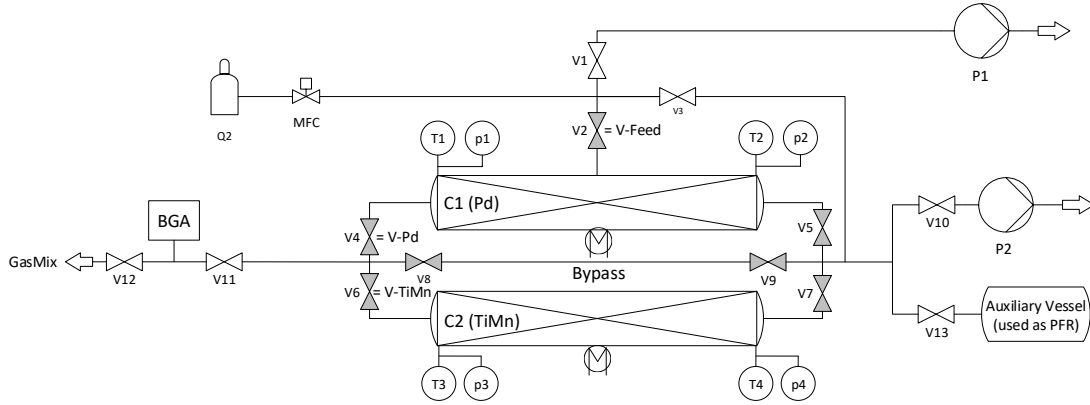


Figure 4.2: Flow sheet of the laboratory set-up HESTIA utilized for $\text{H}_2\text{-D}_2$ separation experiments. Valves highlighted in grey scale equal valves shown in Figure 2.4b) and are essential for process control. Note: Depending on the experiment procedure, a combination of V5, V7, V8 and V9 provide the functionality of the exchange valve V-Exch between the columns. Explanation of components are detailed in the text.

each column to enable controlled pressure relieve in the exhaust pipeline in case of sudden pressure increase. Gas transfer between the columns and feed supply or sample taking is realized by pneumatic bellows valves (V1 to V13) (*Swagelok, SS-12BG-MM-5CM*) controlled by the *human machine interface* (HMI) (c.f. Subsec. 4.1.2). To protect the pressure gauges and the valve seats from mechanical damage caused by material deposition, filters of $2\mu\text{m}$ mesh size (*Swagelok, SS-12TF-MM-LE*) are installed. A list of the utilized sensor uncertainties can be found in Table B.2 in the appendix.

Volume and Temperature Calibration

As described for the set-up MAIA in Subsection 3.1.1, volume and temperature calibrations are necessary to allow for calculation of the absorbed amount of hydrogen in the material bulk during separation experiments. Similar calibration procedures were utilized. The resulting gas volumes are given in Table 4.1, while the effective gas temperature establishing for varying set-point temperatures is shown in Figure 4.3.

As can be seen from the quasi similar lines, the column filling does not impact the observed mean gas temperature. The bend at around 23°C is a result of switching from chiller to oil bath heating power. Remarkable is the distinct deviation between inner gas temperature and set-point temperature. A first conclusion can be drawn from this result: The chosen column geometry needs improvement for future test facilities. Absorption columns shall be completely insulated to reach set-point temperatures. Thus, sensors either have to show appropriate heat resistance or have to be placed at the columns ends outside the insulation.

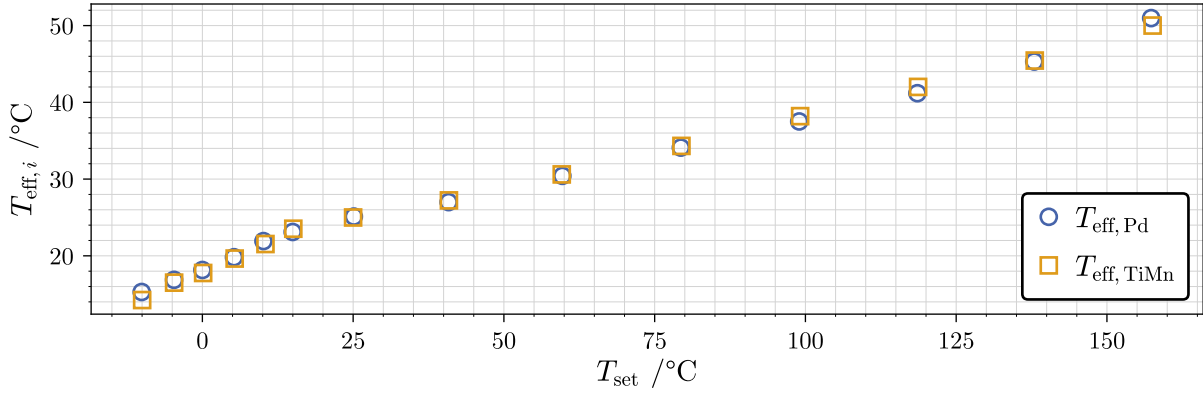


Figure 4.3: Correlation of effective gas temperature establishing within each absorption column with respect to the set-point temperature targeted by the heating and cooling system. Error bars are smaller than the symbols.

Auxiliary Vessel (used as PFR)

To enable separation experiments for single separation efficiency evaluation, an inert auxiliary vessel is installed between the columns separated by an additional pneumatic bellows valve. The gas sample cylinder (*Swagelok, 316L-HDF4-2250*) of 2.25 L is filled with inert Kieselguhr (*Merck Chemicals GmbH*) and allows for imitating TCAP experiments, as it serves as simplified inert PFR of 44 mm in diameter and 100 mm in length. Another operation method using this vessel is the rearrangement of gas profiles, as tested in [26].

Coupled Absorption Materials

Each column centre pipe is filled with absorption material. The amounts of active absorption materials were adapted to each other, such that each absorption column is able to absorb equal amounts of hydrogen. In column 1 (C1), in the following denoted as Pd column, a total mass of 9.13 g Pd supported on 40 g of inert Al_2O_3 spheres of $d_p = 0.8$ mm was filled. In addition, an inlet bed using uncovered Al_2O_3 spheres of the same size was realized which is located at the non heated column ends.

The filling of the TiMn column (C2) was more complex. First, the $\text{TiMn}_{1.5,\text{mod}}$ granulates were grounded. Since the absorption capacities of both columns need to be adapted to each other, the required amount of $\text{TiMn}_{1.5,\text{mod}}$ is limited by the amount of Pd filled into C1. In there, 70 % of the bed is inert material, which means that the TiMn column cannot be completely filled using only active $\text{TiMn}_{1.5,\text{mod}}$. However, no compact bulk bed in turn lead to moving $\text{TiMn}_{1.5,\text{mod}}$ material through the column (as observed during the demonstration campaign) and thus a gas bypass suppressing the envisioned chromatographic separation effect. Therefore, crushed $\text{TiMn}_{1.5,\text{mod}}$ was mixed with Al_2O_3 spheres although

this improvised auxiliary bed does not fully avoid movement of pulverized $\text{TiMn}_{1.5,\text{mod}}$ particles after activation. Therefore, to prevent trapping of $\text{TiMn}_{1.5,\text{mod}}$ particles in the filter elements outside the heating zone, those dead volumes were filled with stainless steel 316L powder of 5 μm mesh size. As this steel type is already used as constructive material, inert behaviour towards hydrogen is assumed and therefore no impact on the separation efficiency is expected. In future, effort is foreseen to optimize the formulation form of $\text{TiMn}_{1.5,\text{mod}}$ by developing a composite comparable to the utilized Pd bulk. By this described approach a total of 4.76 g $\text{TiMn}_{1.5,\text{mod}}$ in combination with 67.3 g inert material (29.3 g of Al_2O_3 and 38 g of 316L powder) was filled into the column.

After filling the columns with Pd and $\text{TiMn}_{1.5,\text{mod}}$ respectively, the piping system and columns were checked concerning their leak tightness, as a contact to air contaminates, inhibits and in the case of $\text{TiMn}_{1.5,\text{mod}}$ even irreversible suppresses the hydrogen absorption capability (c.f. Subsec. 2.1.1). Therefore, a leak detector was used to analyse the integral leak rate of the set-up using helium. An integral leak tightness of 10^{-9} mbarl/s was proven, which is sufficient for the process.

Table 4.1: Material amounts filled in absorption columns and respective column volumes obtained by calibration. Uncertainty of mass = $1 \cdot 10^{-5}$ as scale was calibrated using calibration weights.

Material	m_{mat} [g]	m_{inert} [g]	N_{mat} [mol]	V [mL]
Pd	9.13	40	0.0858	195.32 ± 0.22
$\text{TiMn}_{1.5,\text{mod}}$	4.76	67.30	0.0881	197.61 ± 0.63

4.1.2 Auxiliary Systems

Gas Supply

The lab set-up is connected to a gas storage system delivering Argon (6.0, purity = 99.9999%, *AirLiquid*), Nitrogen (6.0, purity = 99.9999%, *AirLiquid*), Protium (purity = 99.9999%, *AirLiquid*), Deuterium (purity = 99.9%, *AirLiquid*) and an equimolar $\text{H}_2\text{-D}_2$ -mixture (*Linde*). A pressure reducer (*Swagelok*, *CS-STUGT-2018-0189*) is installed to regulate a suitable input pressure of 4.5 bar maximum. Two mass flow controllers (*MKS instruments*, *GE50A*, operation range 2 - 20 sccm and 2 - 1000 sccm) allow for controlled gas feed. The feed column can be selected by opening the respective hand bellows valve installed at each column's mid (c.f. Fig. B.3 and B.4).

Heating and Cooling System

To provide the heating and cooling power for the temperature swings two oil baths (*Huber, CC-208B*, operation range 25 to 200 °C) and a chiller (*Huber, Unichiller 025*, operation range -10 to 40 °C) are used. The oil baths provide a heating power of 7 kW, while the chiller delivers 8 kW cooling power. Both operate with a silicon thermostable oil (hereafter referred to as *thermooil*) (*Greif Laborlösungen GmbH, SilOil M20.195/235.20*, operation range -20 to 195 °C), serving as heating and cooling media in the combined heating and cooling circuit. The thermoil is cycled through the facility by pumps housed in the baths and chiller, respectively. The columns are surrounded by milled heat-resistant duroplastic plates (*Dotherm GmbH, Pressterm WD 25-1*), which serve as double-walled heat exchanger. The pipes and plates are insulated by glass wool and mineral rock wool. The oil level in each system is monitored by swim level switches.

Pumping System and Exhaust

Two vacuum pumps are installed within the HESTIA set-up. For pressures up to 1 bar, the system can be evacuated by a remotely controlled scroll pump P2 (*Edwards, nXDS10i*). For low final pressures of 10^{-9} mbar, a turbo molecular pump P1 (*Edwards, TS85D1001*) is used. As this pump only tolerates inlet pressures of maximum 3 mbar, a hand bellow valve is mounted before its inlet adapter which allows for adjusting the gas flow to be routed to the pump. If pressures to be reduced are above 1 bar, a venting valve allows for pressure driven evacuation directly to the exhaust pipe system. Backflows to the facility are suppressed by an installed check valve.

Process Control and Monitoring

To control all mentioned components like valves, mass flow controllers and the heating and cooling system remotely, a programmable logic controller (PLC) *Siemens* is used. The software *ProfiMessage, Delphin* allows for implementation of automated valve closing and opening actions to provide system safety and allows for data acquisition. For this, sensor output signals are collected by PLC system channels. The HMI *Siemens, WinCC* allows for controlling valve positions, flow and temperature settings and monitoring of the progression of process operation parameters during an experiment, while sensor data is visualized online using the software *ProfiSignal, Delphin Technology*.

4.1.3 Analytics

To evaluate establishing product enrichments reached by a separation experiment, two gas analysis technologies are used. While the mass spectrometer (MS) is a well-established method to analyse very small gas samples on a high precision level, the utilization of a binary gas analyser allows for instantaneous non destructive analysis of a binary gas sample. The utilized devices are presented in the following.

Mass Spectrometer

A short introduction to the general MS measurement principle is given in the appendix (c.f. Subsec. B.2.2). A quadrupol MS (*Pfeiffer, HiQuad and QMA410*) is connected to HESTIA. The sampling is done by a dosage valve until ~ 30 mbar establish in a vessel ($V = 125.85 \pm 0.6$ mL). At this pressure and piping diameters of 4 mm the Knudsen number is < 0.01 , thus a viscous gas transport is realized which is isotope independent (no change in sample composition). Expanding this gas portion in expansion vessels ($V = 1097.44 \pm 1.51$ mL) guarantees for a constant sample composition, while further reducing the pressure. Routing this sample through an orifice of $20 \mu\text{m}$ reduces the pressure to 1 to $5 \cdot 10^{-5}$ mbar in the MS chamber, allowing for utilization of the robust faraday cup for ion detection.

For correlating the measured ion currents to the isotopic compositions, a calibration is required. For this, the equimolar $\text{H}_2\text{-D}_2$ gas mixture is used. However, as the utilized MS only allows for a one point calibration, for reaching low measurement uncertainties, it is strongly advised to analyse sample compositions close to the calibration composition. Since HESTIA experiments deliver two contrary enriched fractions, this cannot be realized. Especially for highly enriched fractions (which are targeted in a CMH-TSA process), MS analysis may cause high uncertainties. Therefore, spectra scans from $m/z=0$ to $m/z=40$ (argon) shall verify the absence of further species like nitrogen, oxygen, water or argon (rest gas analysis). If the obtained ion currents for the hydrogen masses are 2 to 3 orders of magnitude above the ion currents of residual gas species, the composition measured by the binary gas analyzer is trusted, as only the hydrogen species H_2 and D_2 are dominant in the sample.

Binary Gas Analyzer

The binary gas analyser (BGA) (*Scientific Instrument, BGA244*) is installed at the sampling port at the columns end to serve as inline and almost instantaneous analyzation tool (sampling speed < 1 s). To obtain the sample composition, the composition dependent speed of sound of a binary mixture is exploited. The speed of sound $c_{\text{sos},i}$ is characteristic

for a gas species i at a certain temperature and pressure. For an ideal gas $c_{\text{sos},i}$ follows from

$$c_{\text{sos},i} = \sqrt{\kappa \frac{RT}{\tilde{M}_i}}, \quad (4.1)$$

where κ is the pressure dependent adiabatic index and $\tilde{M}_i$ is the molar mass of the gas species i . In general $\kappa = c_p/c_v = c_p/(c_p - R) = 7/5$ for ideal two atomic gases and their isobaric heat capacity c_p . In a binary mixture, the mean molar mass follows from

$$\tilde{M} = \sum_{i=1}^2 z_i^G \tilde{M}_i \quad (4.2)$$

where z_i^G is the molar fraction of component i in the binary gas mixture. With Eq. (4.2) Eq. (4.1) can be rewritten and the speed of sound for a binary mixture $c_{\text{sos,mix}}$ can be formulated as

$$c_{\text{sos,mix}} = \sqrt{\frac{\kappa RT}{\sum_{i=1}^2 z_i^G \tilde{M}_i}}. \quad (4.3)$$

For a binary mixture of known components, the measurement of $c_{\text{sos,mix}}$ delivers the molar fraction of each component. [98] As the $c_{\text{sos},i}$ for homo-isotopologues differ strongly from each other due to their large difference in molar masses ($c_{\text{sos,H}_2} = 1305 \text{ m/s}$ [99] vs. $c_{\text{sos,D}_2} = 921 \text{ m/s}$ [100]), this measurement technique is very accurate (accuracy 0.5 m/s) to distinguish between varying isotope compositions as investigated by Niemes and Braun [101].

However, this technique exclusively serves for the TSA operated in the HESTIA set-up, as it processes H_2 and D_2 only. A process control in a future IRPR CMH-TSA process is not possible, since six isotopologues are present. In addition, the operation range of the sensor requires a sample pressure of 100 to 150 mbar minimum [101]. Since the measurement chamber has a volume of 130 mL, this is a very large required sample amount in contrast to a MS. The CMH-TSA process operates in this pressure range, therefore the BGA can be applied here, but demands a further analysis technique (in this work the MS) to verify the absence of other (impurity) species.

4.2 Activation of Material Beds

Before performing separation experiments, both column beds are activated according their material specific activation procedure identified in Section 3.2. In addition, a bake-out at 180 °C over night while evacuating the system using the turbo molecular pump was prefixed.

Activation of Palladium Column

To activate Pd by reducing the PdO surface according to Eq. (3.5), the column was heated up to 180 °C in a 1 bar H₂ atmosphere. The bed is then permeated by H₂ flow of 20 sccm for 4 h, followed by keeping a steady pressure atmosphere of 2 bar H₂ for another 2 h. To verify a completed activation, a PCI measurement was performed at room temperature. To realize this, the calibration volume set-up with a combined capacity manometer was used to mimic the pre-vessel of the MAIA set-up (c.f. Sec. 3.1). As the observed H₂ PCI at room temperature revealed similar equilibrium pressure, capacity and PCI curve progression, the Pd bed is considered to be fully activated (c.f. Fig. 4.5).

Activation of TiMn Column

Before beginning the activation treatment, a continuous pressure increase within the TiMn column was observed despite verified leak tightness after switching of the pumps. In fact, an outgassing rate of $\sim 10^{-7}$ mbarl/s at room temperature was measured, which might be caused by residual water, evaporating from the Al₂O₃ or 316L steel powder, as both materials have a large surface. Especially steel is known in vacuum applications for outgassing of water and oxide species [102]. The bake-out was intended to remove these residual species, however, as the material is filled in an elongated narrow pipe and the pump is not directly attached behind the valve, the effective pumping speed of the turbo molecular pump is reduced. In addition, the bake-out temperature could not be further increased to intensify the temperature dependent outgassing rate since otherwise sealing and sensors were threatened to be damaged. The attempt to further reduce residual water species by flushing the column at 180 °C using argon only slightly reduced the outgassing rate (before treatment $2 \cdot 10^{-6}$ mbarl/s). As an external material bulk bake-out in a vacuum oven would demand a filling set-up under inert atmosphere and thus reconstruction of several HESTIA components, it was decided to continue with the activation treatment.

To activate the TiMn_{1.5,mod} bed a 4.5 bar H₂ atmosphere was kept for 24 h in the column at room temperature. This pressure above the equilibrium pressure breaks the oxide layers on the surface. After this treatment, the column was charged for 4 times up to 4 bar using H₂ followed by evacuation between the cycling, thus up to the maximum inlet pressure tolerated by the HESTIA gas dosage system, triggering decrepitation to reach the final particle size of 5 - 15 µm.

As for the Pd column, a PCI was measured. Since the capacity manometer reads maximum pressures of 1.2 bar, the PCI was measured at -10 °C to obtain a complete isotherm for comparison to pre-investigation data (c.f. Subsec. 3.2.4). As can be seen from Fig-

ure 4.4, the resulting H_2 PCI measured in HESTIA differs from the isotherm obtained in the Sieverts' apparatus. Although, deviations of the PCI curves may come from the non-ideal conditions in HESTIA (no cooled pre-vessel, long piping between pre-vessel and sample) and the different sample amounts ($m_{\text{TiMn}_{1.5,\text{mod}},\text{HESTIA}} \gg m_{\text{TiMn}_{1.5,\text{mod}},\text{Sievert}}$), they appear too distinct. $\text{TiMn}_{1.5,\text{mod}}$ as activated in HESTIA shows a reduced absorption capability, higher equilibrium pressures and a more intensified sloping in the plateau-range. Those observations indicate a poisoning of the material or material surface by oxygen species, which is supported by the observation of remaining outgassing rates.

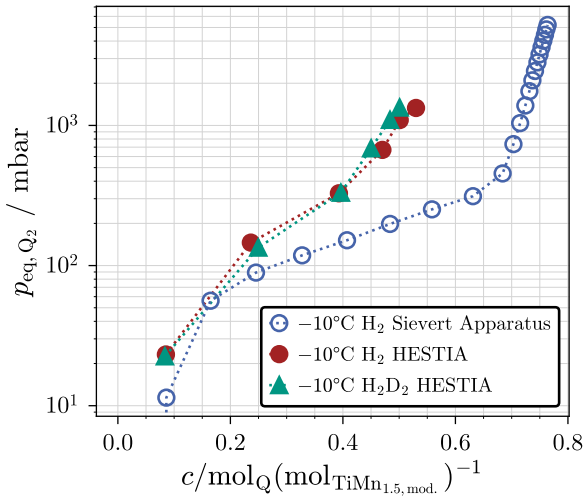


Figure 4.4: Obtained pressure-concentration-isotherms of $\text{TiMn}_{1.5,\text{mod}}$ at $-10\text{ }^\circ\text{C}$ activated in HESTIA in comparison to data observed by Sieverts Apparatus' analysis described in Subsec. 3.2.4. Error bars are smaller than the symbols.

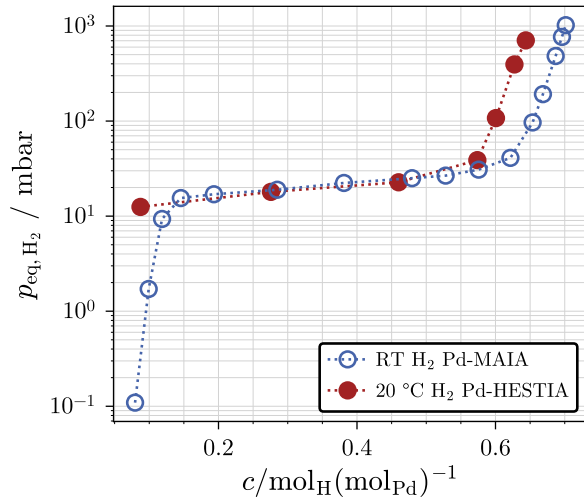


Figure 4.5: Obtained pressure-concentration-isotherms of Pd at $20\text{ }^\circ\text{C}$ activated in HESTIA in comparison to data observed by MAIA analysis (c.f. Subsec. 3.2.1). Error bars are smaller than the symbols.

Additionally, a PCI at $-10\text{ }^\circ\text{C}$ was measured using the equimolar $\text{H}_2\text{-D}_2$ gas mixture to evaluate the separation factor of the poisoned $\text{TiMn}_{1.5,\text{mod}}$ bulk (c.f. green triangle in Fig. 4.4). For a present inverse isotope effect, the proportion of D_2 in the gas phase should lead to lower equilibrium pressures than obtained for the H_2 measurement. Up to a concentration of $c = 0.4$ this is slightly the case, for higher capacities the opposite is observed. The PCI do not clearly support a present isotope effect. Thus an impact of the contamination on the isotope affinity cannot be excluded and is investigated in the following separation experiments described in detail in Subsection 4.3.3 and Section 4.4. Nevertheless, to avoid contamination of absorption material and to allow for more suitable activation treatment in a vacuum oven, in future CMH-TSA set-ups a filling option under inert atmosphere is mandatory. This reconstruction effort is out of scope of this work, therefore the separation experiments were performed using the $\text{TiMn}_{1.5,\text{mod}}$ filling showing non-ideal absorption characteristics.

4.3 Single Column Separation Experiments

The separation efficiency and establishing process parameters, i.e., temperature and pressure, for the different operation steps are investigated for each single absorption column. Especially the results obtained of the Pd column experiments serve as reference for evaluating the impact on the process efficiency and dynamics when using two active separation columns. In addition, the isolated operation of the TiMn column is of interest, to examine the effect of the non-ideal $\text{TiMn}_{1.5,\text{mod}}$ absorption behavior on its separation capability. Furthermore, the influence of the utilized gas exchange route between separation column and auxiliary vessel is investigated to identify the optimal operation mode.

4.3.1 Procedure of Single Column Separation Experiment

Operating one separation column in combination with the inert PFR is comparable to a TCAP (c.f. Subsec. 2.2.1). All mentioned valve numbers are depicted in Figure 4.2, while the described process steps (feeding, temperature switches and gas exchange) orientate on the general CMH-TSA process sequence schematically presented in Figure 2.5. In total, 5 closed cycles are performed during each experiment to promote the evolution of a sharp profile of isotopologue species abundance in the gas phase. The single column operation variants 1, 2 and 3 are schematically shown in Figure 4.6.

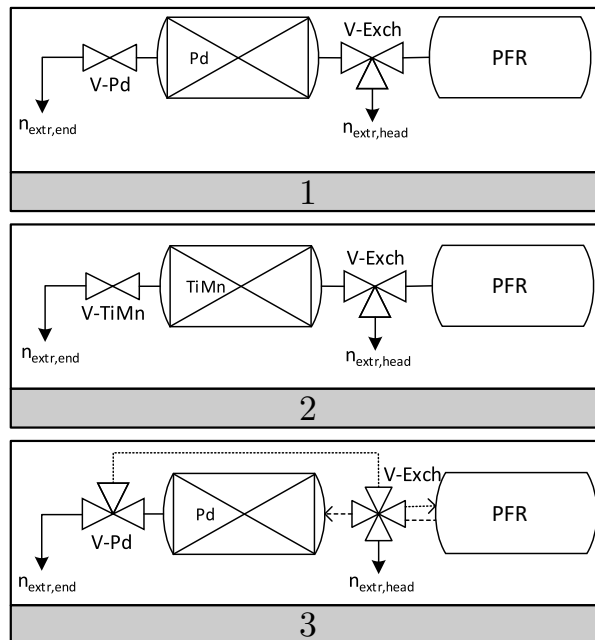


Figure 4.6: Overview of gas exchange variants investigated in HESTIA during single column separation experiments using either the Pd or the TiMn column.

Variant 1 and 2 - Normal Exchange

At the beginning of the experiment, either the Pd or TiMn column is cooled down to the targeted absorption temperature while being evacuated. Due to vacuum conditions the heat conductivity is low, thus this process step requires around 30 min. For a Pd experiment 20 °C are targeted, while for a TiMn_{1.5,mod} evaluation -10 °C are necessary. As soon as no further decrease of the column temperature is observed, the equimolar H₂-D₂-mixture is fed to the columns middle. A feed flow of 200 sccm for approximately 8 min is used until the column pressure reaches 2.5 bar (Pd) or 3.8 bar (TiMn_{1.5,mod}). This equals in both cases a total hydrogen inventory of ~0.052 mol. Independent on the absorption material investigated, the packing has formed a hydride in β -phase region for this amount of hydrogen. After completed feeding, the column temperature is increased to initiate the desorption phase (150 °C Pd and 60 °C TiMn_{1.5,mod}). At the targeted set-point temperature the exchange valves (V5 or V7, V13) are opened until the pressure equilibrates between the column and the PFR. The exchange valves are closed and the column cooled until reaching absorption temperature. Again, the exchange valves are opened and pressure equilibration awaited. The described procedure is repeated for 5 times, such that 5 exchange cycles are performed. The selected operation temperatures are informed by utilising the developed CMH-TSA process model (c.f. Ch. 5) to mimic HESTIA operation and conditions (c.f. Tab. C.1) to fully exploit the reversible plateau-pressure region of each absorption material during cycling.

When reaching the desorption temperature for the fifth time, a product sample is taken from the end of the separation column by opening V4 (Pd) or V6 (TiMn_{1.5,mod}) and V11. The composition is measured using the BGA (c.f. Subsec. 4.1.3). By opening the dosage valve V12, a small portion of this sample is withdrawn to the mass spectrometer to double check the composition and to verify the absence of impurities. After evacuating all attached analysis volumes and flushing the MS chamber using argon, a second gas sample is withdrawn from the columns head pressure driven by opening V5 (Pd) or V7 (TiMn_{1.5,mod}) and V9, V8 and V11. The sample analyse is performed similar to the procedure described beforehand.

Variant 3 - Circular Operation of Pd Column

All experimental steps are similar to the procedure described above, except for the gas exchange route. For depressurizing the Pd column in desorption phase, V4, V8 and V9 (bypass between columns) as well as V11 are opened, thus the gas phase exchanged across the Pd columns end. For the gas transfer from PFR to the Pd column in absorption phase, the valve V5 and V13 are opened similar to the normal operation mode.

After a completed separation experiment all piping, vessels and the column are pumped down using the scroll pump. The desorption temperature is held by the oilbath for 4h while evacuating the column using the turbo molecular pump. Then the heating is switched off and the column is allowed to cool down to room temperature while being further evacuated over night.

Especially for investigations of $\text{TiMn}_{1.5,\text{mod}}$ it was decided to avoid heating up to temperatures above 60°C to not support further outgassing of residual water. To fulfil a similar column treatment after experiments, the Pd column was therefore also not baked-out at temperatures above the utilized desorption temperature.

Determination of Processed Q_2 Amount and Extracted Sample Amounts

To determine the total amount of processed hydrogen mixture for each individual separation experiment, first the total amount of dosed Q_2 $N_{\text{dos,tot}}$ is calculated from the dosing time t_{dos} and the molar feed stream $\dot{N}_{\text{feed}}$ provided by the mass flow controller according

$$N_{\text{dos,tot}} = t_{\text{dos}} \cdot \dot{N}_{\text{feed}} . \quad (4.4)$$

A part of this Q_2 amount is not separated during an experiment, since it remains within the volume of the feed piping $V_{\text{feed-pipe}}$. This non processed amount $N_{\text{feed-pipe}}$ is derived using the ideal gas law and subtracted from $N_{\text{dos,tot}}$:

$$N_{\text{tot}} = N_{\text{dos,tot}} - N_{\text{feed-pipe}} = t_{\text{dos}} \cdot \dot{N}_{\text{feed}} - \frac{p(t_{\text{dos}}) \cdot V_{\text{feed-pipe}}}{RT_{\text{RT}}} . \quad (4.5)$$

In Eq. (4.5) the pressure $p(t_{\text{dos}})$ read by the pressure sensor p2 (Pd column experiment) or p4 (TiMn column experiment) (c.f. Fig. 4.2) after completed feeding time t_{dos} and the room temperature T_{RT} are required. The feed pipe volume $V_{\text{feed-pipe}}$ was determined during volume calibration and equals 186 mL.

The sample extraction is realized pressure driven from the pressured separation column to the evacuated analysis volume $V_{\text{SOS}} = 156.1 \text{ mL}$ of the BGA. To determine the extracted sample amounts for each experiment again the ideal gas law is used:

$$N_{\text{extr,end}} = \frac{p_{\text{SOS}} (V_{\text{SOS}} + V_{\text{extr,end}})}{RT_{\text{RT}}} \quad \text{and} \quad N_{\text{extr,head}} = \frac{p_{\text{SOS}} (V_{\text{SOS}} + V_{\text{extr,head}})}{RT_{\text{RT}}} . \quad (4.6)$$

In Eq.(4.6) $N_{\text{extr,end}}$ refers to the product fraction sampled from the column's end, while $N_{\text{extr,head}}$ equals the product fraction extracted from the column's head, i.e., at the exchange valve. The piping volumes $V_{\text{extr,end}} = 45.5 \text{ mL}$ and $V_{\text{extr,head}} = 187.2 \text{ mL}$ transferring

the sample to the BGA chamber V_{SOS} differ for the extraction ports. This is because the sampled amount of the head product is routed via the bypass between both columns (c.f. Fig. 4.2). The required pressure value p_{SOS} is provided by the pressure sensor installed within the BGA.

The performed single separation experiments and corresponding product composition results are listed in Table 4.2, summarizing the utilized absorption and desorption temperatures, cycle numbers, processed hydrogen inventory and the proportion of extracted product samples. Since the evaluation of the obtained mass spectrometer spectra verified absence of impurity species within all product samples, all presented product compositions are measured by the BGA.

Table 4.2: Overview of measured product compositions, extracted sample amounts and utilized operation parameters of performed single separation experiments using an equimolar $\text{H}_2\text{-D}_2$ feed composition. Schematic description of investigated variants are given in Figure 4.6.

Variant	n_{cyc}	ΔT [°C]	N_{tot} [mol]	$\frac{N_{\text{extr,end}}}{N_{\text{tot}}}$	$z_{\text{H}_2,\text{end}}^{\text{G}}$	$\frac{N_{\text{extr,head}}}{N_{\text{tot}}}$	$z_{\text{H}_2,\text{head}}^{\text{G}}$
1	5	20 - 150	0.0541	7.4 %	0.263	5.9 %	0.545
2	5	-10 - 60	0.0511	3.5 %	0.519	6.3 %	0.511
2	8	-10 - 60	0.0521	3.0 %	0.506	8.0 %	0.510
3	5	20 - 150	0.0534	6.9 %	0.423	8.9 %	0.522

4.3.2 Single Separation Efficiency of Palladium Column

Normal Exchange (Variant 1)

A total hydrogen inventory of 0.0541 mol is processed, which causes a pressure of 2530 mbar after completed feeding at 20 °C. Switching the column temperature to 150 °C results in a pressure increase, which immediately follows the temperature evolution, underlining the fast sorption kinetics. After 13 min, the desorption temperature is reached. Due to heat losses a material temperature of around 142 °C instead of 150 °C establishes. However, the deviation between both thermocouples at each columns end only differ by 1.5 to 2 °C, i.e., no significant temperature distribution is observed. In the case of absorption, temperatures of 20 °C were obtained.

The repeated gas exchanges between column and PFR result in almost instantaneous pressure equilibration, again underlining the fast desorption and absorption kinetics and furthermore the high permeability of the packed bed. Therefore, only 60 s were required for the gas transfer. For exchanges from Pd to the PFR a pressure of around 480 mbar established, while 235 mbar were observed for exchanging the other way round. For the absorption phase, pressures of 30 mbar were measured. During desorption, 2300 to 2420 mbar

depending on the deviation to the set-point temperature and the exchange direction. Since these pressure re-establish for each repeated cycle with minor deviations of maximum 2.1 %, stable and reproducible Pd sorption behavior can be concluded.

After five cycles 0.004 mol (equals 7.4 % of total inventory) were extracted from the end of the column, having a molar protium fraction of 26.29 %. This equals an enrichment of 47.4 % in D₂. On the column's head a sample amount of 5.9 % of the total inventory (equals 0.0032 mol) was extracted revealing a molar protium fraction of 57.45 % thus an enrichment of 14.9 % in H₂. Since Pd preferably absorbs light isotope species it is not surprising, that the enrichment in the non favored species is more distinct, as H₂ is absorbed by the lattice all over the column preferably.

Heung et al. report obtained product purity of > 98 % in both fractions reached during their TCAP experiments. However, to obtain these purifications, around 10 cycles were required and cryogenic temperatures of -75 °C (Pd column) and -190 °C (molecular sieve) were used. In this temperature range the separation factor of Pd is maximized (c.f. Subsec. 2.1.3). In addition, a Pd columns length of 6.35 m was utilized in these experiments, enhancing the chromatographic effect. Therefore, the here presented separation efficiencies are significantly lower in comparison. [35]

Nevertheless, from this experiment the normal isotope effect and separation capability of the Pd column was confirmed and reference values for comparison to a two column experiment obtained.

Circular Operation of Palladium Column (Variant 3)

This gas transfer variant was investigated to evaluate the impact of respecting the establishing gas profile while cycling a hydrogen isotope mixture. Thus, it is analysed if the transferred established gas composition profile can enhance the separation efficiency as schematically shown in Figure 4.7. To do so, instead of depressurizing the Pd column in desorption phase by opening the transfer valves V5 and V11 between column and PFR, V4, V8 and V9 at the columns end were opened and the gas phase transferred over the columns bypass to the PFR (c.f. Fig. 4.2). The gas exchange from auxiliary vessel to the Pd column was not modified.

For the circular single column separation efficiency evaluation of Pd 0.0534 mol were processed performing 5 cycles in total. After feeding a pressure of around 2525 mbar established at 19 °C material temperature which increased to 3550 mbar (desorption pressure) after heating up for 20 min to 143 °C. During depressurizing the Pd column an equilibration pressure of 430 mbar was observed. This is 10.4 % less than during the normal exchange (Variant 1) and results from the larger bypass pipeline volume. On the contrast, during exchange from PFR to Pd column a pressure of 211 mbar results (also 10.2 % less).

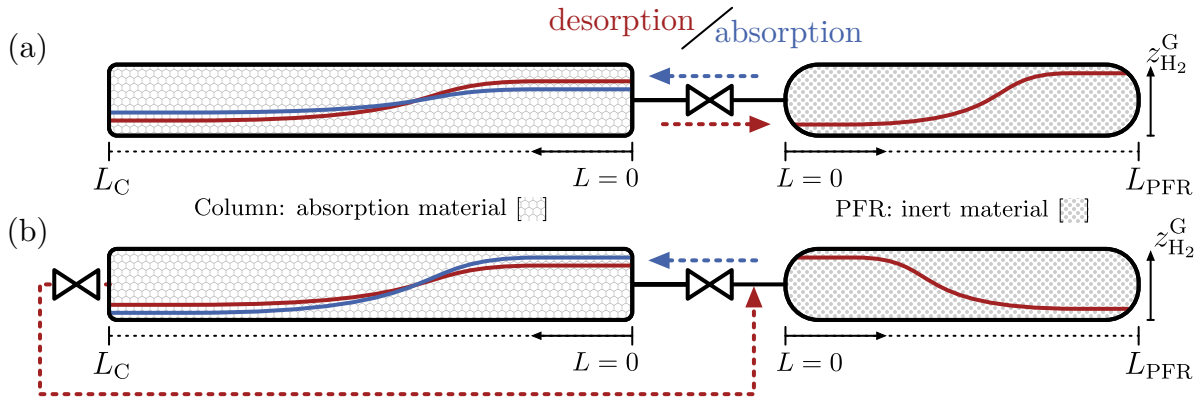


Figure 4.7: Schematic description of the assumed impact of gas phase exchange on the reachable composition profile within the separation column. A detailed explanation is given in the text.

Thus, it should be noted that a slightly reduced hydrogen amount is cycled, as 3 to 6 % of the total inventory remains in the exchange piping in contrast to 0.7 to 1.5 % during normal exchange. However, as the auxiliary vessel contains 39.5 % of the total inventory, the larger piping is not expected to significantly impact the reachable separation efficiency, thus the observed difference is caused by the operation variant itself. Nevertheless, the differing piping is reflected by the reduced process pressures during absorption and desorption. While still 30 mbar are measured during absorption phase (operation in plateau region) a reduced desorption pressure of 2230 to 2300 mbar is observed. After completing 5 cycles an enrichment of 15.4 % in D_2 is achieved from the 0.0037 mol sample extracted from the columns end. On the other side, an enrichment of 4.4 % in H_2 was measured.

Comparison of Exchange Variants

Comparing the observed enrichments of both single separation experiments it can be seen, that a circular operation of the Pd column does not support the separation efficiency but rather reduces it. This leads to the conclusion, that the orientation of the transferred gas profile is irrelevant, and a modification of the exchange route is not effective. The phenomenon can be explained by the occurring isotope exchange reactions. These trigger the replacement of already bounded, less preferred isotope species in the lattice by the favored species (displacement chromatography [56], as shown in Fig. 2.3). When the gas phase is drawn off from the column's end, absorbed isotope atoms emerge from the lattice driven by the equilibrium. Since at the Pd columns head the favored species, i.e. H_2 is bounded, the gas phase is enriched in H_2 . The gas flow is routed from columns head to columns end and contains both isotope species dependent on the equilibrium and the position within the column. The same displacement effect which enhanced the separation during loading the Pd column in absorption phase is now inevitable counteracting the

enrichment. Absorbed D_2 species at the columns end are now replaced by the favored H_2 species due to isotope exchange reactions, which causes the lower enrichment in the protium product in comparison to the normal exchange. Thus the established (sharp) gas composition profile over the columns length is weakened during this exchange variant. However, this demonstrates the dominance of the gas chromatographic effect establishing during gas flows through the columns on the separation efficiency.

4.3.3 Single Separation Efficiency of TiMn Column

Normal Exchange - 5 cycles (Variant 2)

As the PCI investigation of the $TiMn_{1.5,mod}$ bulk filled in HESTIA reveals deviations to the ideal behavior (c.f. Fig. 4.4), the lowest achievable temperature which can be realized in HESTIA ($-10^\circ C$) is selected as absorption temperature to exploit the maximal capacity and separation efficiency. A total amount of 0.521 mol of the equimolar H_2 - D_2 mixture was fed with 200 sccm into the cooled TiMn column (material temperature due to heat losses were $-7.5^\circ C$) leading to a pressure of 3025 mbar. The concentration of isotopes in the $TiMn_{1.5,mod}$ lattice after feeding was calculated to be $0.546 \text{ mol}_Q/\text{mol}_{TiMn_{1.5,mod}}$, thus less than the measured capacity in the Sieverts' Apparatus (c.f. Fig. 3.9). After heating the column to $56.5^\circ C$ (set-point target $60^\circ C$) a pressure of 3752 mbar established. The difference between both temperature sensors was $0.5^\circ C$ maximum for the whole experiment, thus no considerable temperature distribution along the column was observed.

During the exchange from the TiMn column to the auxiliary vessel an equilibration pressure of 410 mbar establishes, while 310 mbar results the other way round. In the case of Pd larger differences between those exchange pressures were measured, underlining the lowered absorption capability of the $TiMn_{1.5,mod}$ filling. In addition, in comparison to the Pd single evaluation, longer exchange times of at least 3 min are necessary. This follows from reduced desorption and absorption kinetics of $TiMn_{1.5,mod}$, which supports the assumption of poisoned $TiMn_{1.5,mod}$ surface, inhibiting the hydride formation reaction.

At $-7.5^\circ C$ an absorption pressure of 70 to 80 mbar establishes while desorption pressures of 1150 mbar are observed. Those pressure amplitudes differ only by 4.6 % during the repeated cycles supporting reproducible absorption and desorption behavior. Thus it can be summarized, that $TiMn_{1.5,mod}$ does reversibly absorb hydrogen, but shows reduced capacities and inhibited sorption kinetics.

Nevertheless, the composition of the 0.0018 mol sample at the column's end revealed a molar protium fraction of 0.519, thus only an enrichment in protium of 3.8 %. On the other column side, even more surprisingly, also an enrichment in protium of 2 % was obtained. By theory, here, an enriched fraction in D_2 should be withdrawn instead. As the composition is almost similar, the questions come up, if $TiMn_{1.5,mod}$ a) absorbs at all and

b) if so, shows an isotope preference.

Question a) is answered immediately, since all characteristics occurring during hydride formation are observable: pressure decreases over time, the calculation of the processed hydrogen inventory reveals a delta in the gas phase comparing to the amount fed, thus hydrogen has to be stored in the lattice and finally also the characteristic heat release during hydride formation is observable by a temperature increase during exchange. However, even though no gas profile is measured, at least a slight enrichment of H_2 is observed showing that a larger quantity of D_2 is absorbed in the solid phase, supporting the existence of an inverse isotope effect. However, in comparison to the PCI data of $TiMn_{1.5,mod}$ described Subsection 3.2.4 and regarding the distinct separation efficiencies observed for the Pd column, this separation effect is remarkably reduced.

Normal Exchange - 8 cycles (Variant 2)

Since the isotope effect of $TiMn_{1.5,mod}$ is not as distinct as the one of Pd as can be seen in the van't Hoff plot in Figure 3.11, the experiment was repeated performing 8 cycles, to further enhance the establishment of a gas composition profile over the columns length or to verify a loss of separation efficiency.

0.0521 mol of hydrogen were processed, leading to a pressure of 3115 mbar after feeding, which increased to 3800 mbar when raising the temperature to 60.5 °C. Also the pressures during the repeated process steps were in the same order of magnitude as the above described 5 cycle investigation. Nevertheless, when extracting 3 % of the total molar inventory from the columns end, again only 1.2 % enrichment in H_2 were measured. The analysis from the head sample (8 % of total inventory) revealed a H_2 enrichment of 2 %.

From this experiment follows, that obtained product compositions withdrawn from the TiMn column are not affected by the number of TSA cycles, which is not reasonable according to the process theory. For ideal $TiMn_{1.5,mod}$ behavior, the product enrichment would increase for more performed closed cycles. Nevertheless, a slight enrichment in H_2 was observed, reflecting a weak inverse isotope effect. However, since in both product fractions this weak and furthermore almost similar enrichment in H_2 was measured, it is assumed that $TiMn_{1.5,mod}$ serves as *single separation stage*, i.e., does not exploit the gas chromatographic effect (multi-separation-stages). The latter would cause an opposite isotope composition in the sampled product fractions, as it is the case for the Pd column (c.f. Subsec. 4.3.2). The following separation experiment variations using both absorption columns can be understood as *diagnose experiments*, to further identify the reason(s) for limited separation and absorption efficiency observed for the TiMn column.

4.4 Two Column Separation Experiments

Separation experiments exploiting the coupled Pd and TiMn column intend to evaluate if the CMH-TSA process is optimized by introducing a second active separation column filled with material showing an inverse isotope effect than Pd. However, as $\text{TiMn}_{1.5,\text{mod}}$ filled in HESTIA does not provide its ideal absorption characteristics, the performed combined column separation experiments serve for identifying the present $\text{TiMn}_{1.5,\text{mod}}$ state and characteristics in the absorption column, causing the loss in separation capability, and to provide data for comparison to HESTIA simulations using the developed CMH-TSA model (c.f. Subsec. 5.3.4). First, the experimental procedure and the exploited operation variants are presented, followed by discussion of the obtained results.

4.4.1 Procedure of Two Column Separation Experiments

Three operation variants of a separation experiment using the Pd and the TiMn column were analyzed. They are schematically given in Figure 4.8, referred to as Variant 4, 5 and 6. Utilized valve numbers are assigned in the HESTIA flow sheet given in Figure 4.2. As described for the single column separation procedure in Subsection 4.3.1, 5 closed cycles are operated in each experiment including process steps analogue to a CMH-TSA process routine introduced in Figure 2.5. Selected absorption and desorption temperatures for each material equal those chosen for the corresponding single column separation to provide similar conditions.

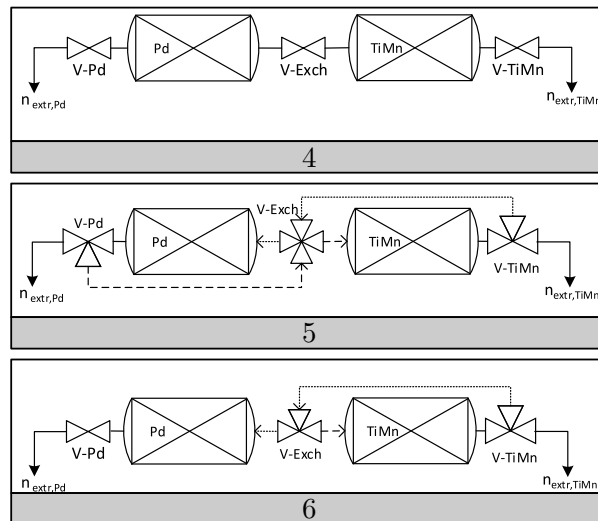


Figure 4.8: Overview of gas exchange variants investigated in HESTIA during separation experiments using both columns.

Variant 4 - Normal Operation

The procedure of a separation experiment using both columns is almost similar to a single column separation test (c.f. Subsec. 4.3.1). Each experiment starts by cooling the Pd column to its targeted absorption temperature of 20 °C. Then the equimolar H₂-D₂-mixture is fed into the Pd columns middle for ~8 min using a 200 sccm flow rate, resulting in a pressure of ~ 1.5 bar. While heating the hydrided Pd column to a desorption temperature of 120 °C, the TiMn column is cooled to -10 °C. After each set-point temperature is reached, the first pressure driven gas transfer is allowed by opening the exchange valves V5 and V7 between the columns. Pressure equilibration is reached after around 3 minutes, then the valves are closed and the set-point temperatures are changed ($T_{\text{Pd}} = 20\text{ °C}$, $T_{\text{TiMn}_{1.5,\text{mod}}} = 60\text{ °C}$). A gas exchange is allowed again after the target temperatures establish. This procedure is repeated 5 times, such that 5 complete cycles are performed.

After reaching desorption temperature for the fifth time, V4 is opened at the end of the Pd column and a product sample is withdrawn, which is analyzed by the BGA and MS. The remaining gas phase in the Pd-column is transferred pressure driven to the TiMn column in absorption phase (cooled) by re-opening V5 and V7. Then the TiMn column is heated to its desorption temperature. The evacuated and flushed analysis chambers are filled with a sample withdrawn from the end of the TiMn column (opening V6). The post-processing treatment after each separation experiment is similar to the procedure of a single column separation experiment (c.f. Subsec. 4.3.1).

Variant 5 - Gas Exchange over Columns End

The gas transfer routing between both columns is varied. When exchanging the gas phase from the Pd column to the TiMn column, V4 at the end of the Pd column is opened and the pressure driven gas flow guided across the bypass (V8, V9 and V7 opened) in the head of the TiMn column. Analogue to that, V6, V8 and V9 are opened to transfer the gas phase from the end of the TiMn column to the head of the Pd column (V5) in the contrary direction.

Variant 6 - Circular Operation of TiMn Column

This variant operates the TiMn column in a circular mode, thus the gas transfer from Pd to TiMn column is realized similar to the normal operation mode (Variant 4), while the gas route analogue to Variant 5 is utilized when exchanging from TiMn to Pd column.

Determination of Processed Q_2 Amount and Extracted Sample Amounts

The processed amount of hydrogen N_{tot} is calculated similar as described for single separation experiments in Eq. (4.5) by the dosing time t_{dos} , molar feed rate $\dot{N}_{\text{feed}}$ and remaining Q_2 amount in the feed pipelines $N_{\text{feed-pipe}}$. The product sampling is realized pressure driven at the end of each column respectively. Therefore, the extracted product amount N_{extr} follows from Eq. (4.6) using the piping volume $V_{\text{extr,end}}$.

Similar to the single column separation efficiency investigations, the analyzed gas samples were only composed of hydrogen isotope species, as the MS measurements confirmed. The given enrichments are therefore obtained from speed of sound measurements. All discussed coupled column experiments, the explored process temperatures, processed hydrogen inventories and extracted sample amounts as well as obtained product compositions are listed in Table 4.3.

Table 4.3: Overview of process parameters, observed enrichments and extracted sample amounts for investigated process variants using both HESTIA separation columns. For each experiment, an equimolar $\text{H}_2\text{-D}_2$ feed composition was used and 5 cycles in total were performed before product extraction. Selected column temperature amplitudes equal those of the respective single separation experiments (c.f. Tab. 4.2). Schematic description of variants are given in Figure 4.8.

Variant	N_{tot} [mol]	Column	ΔT [°C]	$\frac{N_{\text{extr}}}{N_{\text{tot}}}$	$z_{\text{H}_2}^{\text{G}}$
4	0.0537	Pd	20 - 150	8.4 %	0.334
		TiMn	-10 - 60	6.3 %	0.570
5	0.0535	Pd	20 - 150	8.2 %	0.455
		TiMn	-10 - 60	5.6 %	0.487
6	0.0537	Pd	20 - 150	7.8 %	0.353
		TiMn	-10 - 60	5.8 %	0.569

4.4.2 Pd - TiMn_{1.5,mod} Normal Operation

In this operation mode, the columns are heated oppositely and exchange the establishing gas phase over the exchange valve placed between both columns (Variant 4 in Fig. 4.8). The same process temperatures are utilized as in the single column separation experiments described in Section 4.3, thus -10 to 60 °C (TiMn_{1.5,mod}) and 20 to 150 °C (Pd).

A total hydrogen inventory of 0.537 mol of the equimolar $\text{H}_2\text{-D}_2$ -mixture was fed into the cooled Pd column resulting in a pressure of 2513 mbar. This pressure increased to 3878 mbar after reaching the desorption temperature of 148 °C. The given pressure values are in the same order of magnitude as obtained during single separation operation of Pd (c.f. Subsec. 4.3.2). The obtained pressures for gas exchange equilibration from Pd

to $\text{TiMn}_{1.5,\text{mod}}$ slightly decreased over the 5 performed cycles starting at 1431 mbar and reducing about 50 mbar each cycle to 1260 mbar finally. On the contrary, almost equal equilibration pressures of 790 mbar established when exchanging from the $\text{TiMn}_{1.5,\text{mod}}$ bed to the Pd packing. The absorption capacity of $\text{TiMn}_{1.5,\text{mod}}$ appear to slightly increase with each absorption step, thus does not support stable material characteristics. Pd in contrast shows reproducible and reversible absorption behavior, i.e., withdrawal of equal hydrogen amounts from $\text{TiMn}_{1.5,\text{mod}}$ represented by similar absorption pressures over the cycles. From this observation can be concluded, that the Pd packing is not affected or contaminated by the gas exchange with the TiMn column, thus the impurity species are bounded on the $\text{TiMn}_{1.5,\text{mod}}$ surface.

The time necessary for completed gas exchange of 3 min is limited by the TiMn column. Thus, $\text{TiMn}_{1.5,\text{mod}}$ sorption kinetics are slower than those of Pd, which was also observed during MAIA experiments. The obtained absorption pressures of Pd over the cycling are 30 mbar (plateau-region, c.f. Fig. 3.4) and 2800 mbar during desorption. $\text{TiMn}_{1.5,\text{mod}}$ pressures alternate between 180 mbar for absorption, lowering to 130 mbar for time advanced cycles and reaches 2440 to 2500 mbar during desorption. As expected from the PCI of both materials, in general, equilibrium pressures of $\text{TiMn}_{1.5,\text{mod}}$ are larger than those of Pd.

After 5 cycles 8.4 % of the total inventory is withdrawn from the Pd column's end. The analysis of the product composition reveals a protium proportion of 33.4 %, thus an enrichment in D_2 of 33.2 %. This is slightly less than observed during single separation experiments of Pd. However, the sample composition withdrawn from the TiMn column's end (6.3 % of total inventory) shows a similar enrichment in protium of 13.4 % (c.f. Tab. 4.2). It should be noted, that the differing sample amounts extracted are caused by the different desorption pressures of the columns. As the sample extraction is realized pressure driven by opening the pneumatic bellow valves to the analysis chamber volume, only a higher process temperature of $\text{TiMn}_{1.5,\text{mod}}$ would allow for an increased sample amount, which is not suitable for the envisioned column's interaction.

Almost similar product compositions were withdrawn from the columns as from the Pd single operation (c.f. Subsec. 4.3.2). It appears that $\text{TiMn}_{1.5,\text{mod}}$ does not contribute to the separation. Instead, it even reduces the enrichment of D_2 on the Pd extraction port (V-Pd) while it supports the enrichment of H_2 on the $\text{TiMn}_{1.5,\text{mod}}$ extraction port (V-TiMn). Beside the slightly larger product amount of 13.5 % withdrawn from the Pd column in comparison to the single Pd column experiment, this phenomenon might be enhanced by the assumed slight inverse isotope effect of the $\text{TiMn}_{1.5,\text{mod}}$ bulk in HESTIA. While the auxiliary vessel is unable to absorb hydrogen, D_2 is stored in the $\text{TiMn}_{1.5,\text{mod}}$ lattice. Thus, the gas phase re-routed to the Pd column is reduced in its D_2 proportion,

as the sorption kinetics of $\text{TiMn}_{1.5,\text{mod}}$ are inhibited. Therefore, the Pd column is more occupied by H_2 species than in the single column operation scenario, leading to a slight reduction in the measured H_2 depletion. However, it is still not clear if these observations are caused by the non ideal behavior of the $\text{TiMn}_{1.5,\text{mod}}$ packing or if an ideal TiMn column would counteract the separation efficiency of the Pd column, too.

4.4.3 Pd - $\text{TiMn}_{1.5,\text{mod}}$ Circular Operation

To verify a single separation stage within the TiMn column, the TiMn column was operated in a circular mode, thus depressurizing the TiMn column across the column's end to the head of the Pd column (Variant 6 in Fig. 4.8). The gas exchange of the Pd column remained unaffected. If $\text{TiMn}_{1.5,\text{mod}}$ serves as single separation stage, no impact on the product compositions should reveal in comparison to the normal operation mode described above, assuming that the impact of the larger bypass piping (c.f. Fig. 4.2) can be neglected.

A hydrogen amount of 0.054 mol was cycled between both columns. For Pd absorption pressures of 30 - 40 mbar in the plateau region were measured, while 2550 mbar established during desorption phase. In the case of $\text{TiMn}_{1.5,\text{mod}}$ absorption pressures of 130 mbar resulted, similar to the absorption pressures obtained during normal operation. In desorption phase, pressures of 2220 mbar established, which are lower comparing to desorption pressures in normal operation. This observation is correlated to the larger bypass volume utilized in this gas route, which adds a further piping volume of 187 mL. When depressurizing the TiMn column over the column's bypass, an equilibration pressure of 640 mbar established. The gas transfer from Pd to $\text{TiMn}_{1.5,\text{mod}}$ over the middle exchange valve revealed an equilibration pressure of 1130 to 1100 mbar instead.

After 5 cycles, 7.8 % of the total inventory is extracted from the end of the Pd column, showing a composition which is enriched by 29.3 % in D_2 . This is almost equal to the product composition extracted during normal operation. A sample amount of 0.003 mol withdrawn by the TiMn column revealed an enrichment of 13.7 % in protium which is identical to the normal operation experiment. Thus, it can be concluded, that indeed the *TiMn column serves as single separation stage* such that no gas profile establishes during operation. Therefore, the gas exchange route either from the TiMn columns head or from the TiMn columns end to the coupled Pd column does not impact the obtained product compositions. This finding is in agreement with the observation of equal product compositions extracted from the TiMn column after 5 and 8 cycles during its single operation (c.f. Subsec. 4.3.3).

The establishment of a single separation stage within the TiMn column can be explained by its packing structure. To enable complete column filling similar to the Pd column

albeit $\text{TiMn}_{1.5,\text{mod}}$ is not deposited on inert carrier material, as an intermediate solution, $\text{TiMn}_{1.5,\text{mod}}$ granulates were mixed with inert Al_2O_3 spheres (c.f. Subsec. 4.1.1). During activation $\text{TiMn}_{1.5,\text{mod}}$ decrepitate to particles of 5 to 15 μm . These particles are smaller than the void spaces between the alumina spheres of 0.8 mm in diameter and trickle through the column packing until they accumulate on the bottom of the columns cross-section. In addition, the pressure peaks during gas exchange between both columns trigger movement of $\text{TiMn}_{1.5,\text{mod}}$ powder in axial direction. Beside the accumulation of active $\text{TiMn}_{1.5,\text{mod}}$, reducing the distribution to exploit the whole columns length, the settling introduces a gas bypass, further reducing the chromatographic separation effect. The described mechanisms are schematically shown in Figure 4.9.

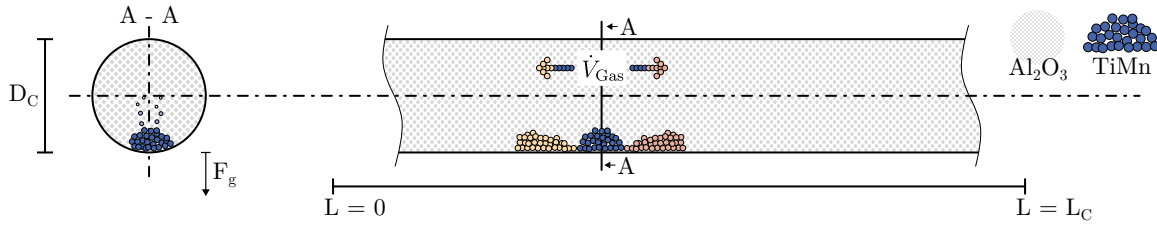


Figure 4.9: Schematic description of assumed $\text{TiMn}_{1.5,\text{mod}}$ powder mobility mechanisms within the HESTIA separation column. Left: $\text{TiMn}_{1.5,\text{mod}}$ powder trickles due to gravity F_g through the inert alumina sphere packing. Right: Axial movement of accumulated $\text{TiMn}_{1.5,\text{mod}}$ caused by gas flows $\dot{V}_{\text{Gas}}$ and introduced gas bypass through inert alumina packing.

4.4.4 Pd - $\text{TiMn}_{1.5,\text{mod}}$ Exchange Variation

To complete the study of gas transfer variation, a separation experiment was performed withdrawing the gas phase from the columns end and feeding into the partner columns head (Variant 5 in Fig. 4.8). This experiment shall allow for evaluation of the impact of respecting the establishing gas profiles during repeated cycling as explained in Figure 4.7 and serves for supporting the conclusion drawn from the single Pd column experiment (Variant 3, c.f. Subsec. 4.3.2), which revealed reduced separation efficiency using this gas route.

While the obtained absorption and desorption pressures of Pd equal those of the normal operation experiment, i.e., 30 mbar and 2750 to 2800 mbar, only the absorption pressures of $\text{TiMn}_{1.5,\text{mod}}$ are unaffected by the modification (130 to 140 mbar). However, the desorption pressure of TiMn was reduced to 2100 mbar, which is closer to the desorption pressure obtained in Variant 6 than 4, and therefore is related to the larger bypass volume. Additionally, for the exchange from Pd to $\text{TiMn}_{1.5,\text{mod}}$ this revealed a pressure of 1000 to 1100 mbar, while 630 mbar were observed in the other direction. Those exchange pressures are almost similar to the circular operation of $\text{TiMn}_{1.5,\text{mod}}$ described in Subsec-

tion 4.4.3.

A sample amount of 0.0044 mol withdrawn from the Pd column exposed a molar protium fraction of 0.455. This refers to an enrichment in D_2 of only 9 % instead of 33.2 % as obtained during normal operation. The withdrawn sample from the TiMn column (0.003 mol) showed a reduced protium content of 0.487, even though on this side an enrichment in protium is to be expected. As already learned from this exchange operation during single Pd operation, the gas transfer respecting the gas profile composition does not enhance the separation efficiency. The utilization of two active separating columns suppresses the separation effect even more. This might also be impacted by the higher amount of not exchanged residual hydrogen in the exchange pipe of up to 14.9 % of total inventory, as during normal exchange only 2.5 to 4 % are remaining in the transfer piping. While the product composition derived by the Pd column is almost equal to those obtained during the Pd single operation exchange variation (Variant 3), the difference in composition between the $TiMn_{1.5,mod}$ sample and the Pd column head product of the corresponding single column experiment is larger. However, due to the pressure driven product extraction the withdrawn product amounts differ from each other (c.f. Tab. 4.2 and 4.3), which could cause these observed deviations. Nevertheless, the reduction in the product enrichment is qualitatively reconfirmed in the coupled column experiment for this gas exchange route.

4.5 Conclusions of HESTIA Operation

The presented laboratory set-up HESTIA allowed for investigating various CMH-TSA operation scenarios using either one active separation column or a column couple. Unfortunately, the $TiMn_{1.5,mod}$ packing activated in HESTIA did not show ideal sorption behavior as measured in Subsection 3.2.4. Therefore, it was not possible to evaluate, if the utilization of two active separation columns increases the obtainable product enrichment of a operated single Pd column, which is stated by hypothesis 2. Instead, a series of diagnose experiments allowed for interpretation of the obtained data and lead to the following two assumptions of the $TiMn_{1.5,mod}$ state in HESTIA:

First, the $TiMn_{1.5,mod}$ filling in HESTIA is contaminated by residual water or oxygen species which were accidentally introduced to the column by the utilized inert materials Al_2O_3 and stainless steel powder. Those were intended to serve as packing structure comparable to the Pd column filling. However, the pre-experimental bake-out and flushing procedure did not completely remove these impurities. Instead, the highly reactive $TiMn_{1.5,mod}$ surface formed during activation immediately reacted irreversible to TiO_2 ,

causing a contaminated surface which inhibited isotope dependent hydride formation. The following observation support this assumption:

- The obtained PCI of the $\text{TiMn}_{1.5,\text{mod}}$ filled in HESTIA showed higher equilibrium pressures and reduced capacity in comparison to PCI characteristics measured in the Sieverts' apparatus (c.f. Subsec. 3.2.4).
- The plateau-region suffered from distinct sloping, an indicator for contaminated alloy surfaces [46, 43].
- The absorption and desorption kinetics are significantly reduced [46].
- A repeated activation treatment did not provide an improvement.

It is not clear, if this contamination impacts the isotope preference determined for the original alloy.

Second, the active $\text{TiMn}_{1.5,\text{mod}}$ material is not distributed uniformly over the columns length. Instead, due to its powdered form after activation it travels through the Al_2O_3 packing triggered by pressure peaks during gas exchange or evacuation. Due to this movement, no permanent separation stages are realized. Although the Al_2O_3 packing partly suppresses this effect, it does not avoid an accumulation. In addition, due to gravity, the $\text{TiMn}_{1.5,\text{mod}}$ powder trickles to the bottom of the column pipe cross-section. This allows for gas bypasses in the upper, non separating cross-section part. This assumption is supported by the following observations:

- Nearly equal compositions were withdrawn at both column ends during single $\text{TiMn}_{1.5,\text{mod}}$ operation, which refers to a single separation stage. This is also supported by a second experiment, in which the circular operation of $\text{TiMn}_{1.5,\text{mod}}$ in combination with Pd lead to the same enrichments as the normal operation mode.
- After de-commissioning, accumulated powder was found in previously non filled parts of the column components.
- A slight inverse isotope effect was observed during single separation evaluation, as both extracted fractions were enriched in H_2 . In addition, the measured $\text{H}_2\text{-D}_2$ PCI (c.f. Fig. 4.4) showed a slight inverse isotope effect, which supports a reduced remaining separation capability despite contamination.

Possibly a combination of both effects lead to the reduced $\text{TiMn}_{1.5,\text{mod}}$ separation efficiency. To further investigate and verify these assumptions, the described HESTIA experiments have been mimicked by the developed CMH-TSA model, which is presented in Chapter 5. The obtained results are discussed in detail within Section 5.3.

Finally, the operation experience gained during the HESTIA campaign serves for informing future CMH-TSA facilities and identification of open points for optimization as described in the following.

4.5.1 Requirements for Future $\text{TiMn}_{1.5,\text{mod}}$ Formulation

To enable a TSA operation using a TiMn absorption column requires optimization concerning the formulation of $\text{TiMn}_{1.5,\text{mod}}$. Especially, future work should be invested in developing a composite, e.g., coating $\text{TiMn}_{1.5,\text{mod}}$ on an inert carrier material as succeeded for Pd. To support this, an absorption experiment in MAIA was performed to verify the suitability of Al_2O_3 for this task in general. In addition, this result is important when considering that $\text{TiMn}_{1.5,\text{mod}}$ interacts indirectly with this inert material in any case due to the gas exchange with the Pd column.

A mixture of $\text{TiMn}_{1.5,\text{mod}}$ and Al_2O_3 -spheres was filled with same mass ratio as used in HESTIA into the sample holder of MAIA. After performing a bake-out at 320°C for 24 h while evacuating the system with the turbo molecular pump, the activation procedure of TiMn as described in Subsection 3.2.4 and 4.2 was performed. Then a PCI at room temperature using H_2 was measured and compared to the result of the pure $\text{TiMn}_{1.5,\text{mod}}$ sample. As can be seen from Figure 4.10, if a sufficient pre-treatment, i.e. bake-out to remove residual oxygen species, of the $\text{TiMn}_{1.5,\text{mod}}\text{-Al}_2\text{O}_3$ -mixture is performed, no influences have to be expected on the $\text{TiMn}_{1.5,\text{mod}}$ absorption behavior, as almost equal equilibrium pressures and capacities are observed. Thus this experiment shows the utility

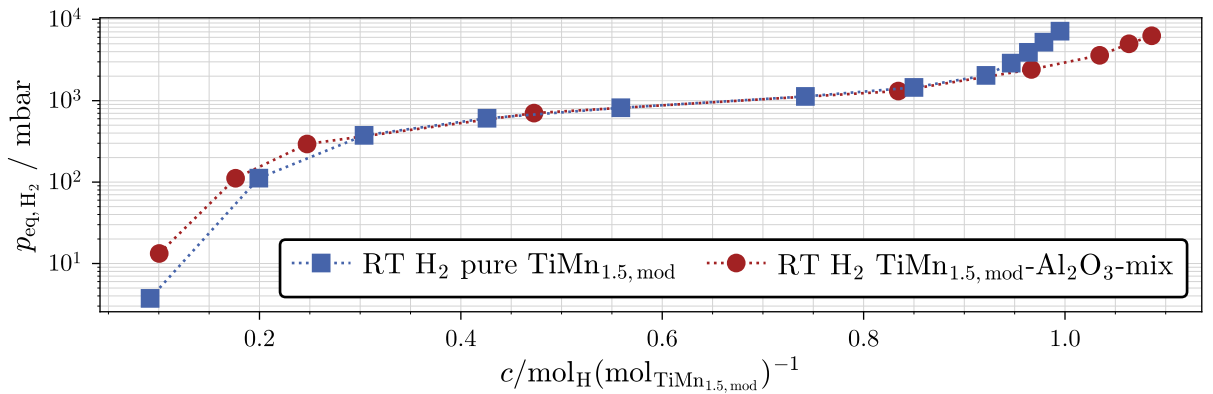


Figure 4.10: Comparison of H_2 pressure-concentration-isotherms at room temperature measured in MAIA of a pure $\text{TiMn}_{1.5,\text{mod}}$ sample and a $\text{TiMn}_{1.5,\text{mod}}\text{-Al}_2\text{O}_3$ -mixture. Error bars are smaller than the markers.

of Al_2O_3 to serve as inert support material in TSA processes. Nevertheless, a suitable pre-treatment procedure is essential for successful process operation. This requires a constructive optimization realising a fill-in of activated material under inert atmosphere.

This enables an ex-situ activation treatment, which exploits higher bake-out temperatures and effective pumping speeds.

4.5.2 Requirements for Future CMH-TSA Set-ups

Beside the above mentioned suggested construction to transfer activated material in the separation columns, further construction issues came up during HESTIA operation, which are listed in the following.

A main drawback of the set-up HESTIA are the sensor ports welded to the centre material carrier pipe. Those ports introduce void spaces in which gas can be accumulated and re-mixed, counteracting the exploited chromatographic effect of separation. Instead, all sensors should be mounted before and after the packing.

Another point of optimization is the insulation of the column. The temperature sensitivity of the capacity manometers utilized in HESTIA did not allow for complete insulation and caused heat losses leading to gas temperature distributions. Again, replacement of the sensors overcomes this issue and significantly reduces the gap between the establishing effective gas temperature and set-point temperature (c.f. Fig. 4.3).

Furthermore, the placement of temperature sensors should be optimized. Due to construction reasons, only the sensor tip is immersed in the material. Thus, a mixture of material, gas and heating media temperature is measured. Instead, thinner Pt100 are suggested with immersion parallel to the column's length axis.

As described in Section 4.3 and 4.4, the sample extraction of both columns was realized pressure driven. The amount of extracted gas sample was determined by the sample expansion volume and the desorption pressure of each column. To allow for controlled sampling below 10 % of the total processed inventory, a dosage valve is suggested.

Filters were placed in front of sensors and valve seats to protect those components of damage by material contact. However, the chosen T-filters introduced trapping volumes for moving material. Therefore, future protection should be realized as in-line filters.

During the experiments the heating and cooling systems revealed to be undersized for the scale of HESTIA. In addition, the combination of both systems lead to counteracting the heating and cooling efficiencies of the oil reservoirs due to mixing of cold and hot oil when switching column temperatures. As the utilized thermooil shows a significant density dependence of temperature over the large temperature differences during the swings, the installed level switches often sound the alarm. Separating the heating and cooling task is advised as well as larger oil reservoirs. Beside this heating rate limitation further optimization can be targeted during material development. Utilizing an inert support material with high thermal conductivity allows for increased heat conductivity and therefore shortens heating times. Those are the main limitations in reachable process times [103].

Chapter 5

Process Model Development of CMH-TSA

To support the CMH-TSA process development and scale-up for the EU-DEMO IRRP application concerning the column design, identification of suitable operation schedules and achievable throughputs, a spatio-temporal process model is developed in this work, which is able to mimic HESTIA experiments and large scale IRPR operation. To cover this broad application range, a robust equation based simulation tool is envisioned, exploiting experimental data for parameter implementation. In this chapter, first the model equations are presented and categorized in sub-models. Additionally, assumptions and simplifications are discussed and the extrapolation to tritium operation is described. Then the parameter derivation and validation of the sub-models by comparison to experimental data obtained by MAIA experiments and HESTIA flow through investigations is presented. The CMH-TSA model validation is completed by simulation of HESTIA experiments and their discussion with the experimental data described in the previous Chapter. In addition, these comparisons allow for interpretation of the state of $\text{TiMn}_{1.5,\text{mod}}$ filled in the HESTIA TiMn column (c.f. Sec. 4.5).

Finally, the developed CMH-TSA process model serves for evaluation whether the TSA separation efficiency is enhanced by coupling to metallic absorption columns (H2), the verification of the inverse isotope effect of $\text{TiMn}_{1.5,\text{mod}}$ (H3) and the capability of fulfilling the separation task for the IRPR system (H1). The latter is targeted in Chapter 6.

Various TSA and TCAP models are described in literature serving to inform hydrogen separation processes about achievable product compositions, suitable column dimensions and heat transfer characteristics, i.e., between column and heating systems and within the packing. Other comparable models are developed to optimize metal hydride storage applications for example concerning loading and deloading times and heat management during

hydride formation. Physics based kinetic models are utilized to investigate for example the establishing heat transfer or the saturation within a hydride bed. Charton et al. developed a model to predict the gas chromatographic isotope separation efficiency of a Pd bed due to isotope exchange reactions [53], while Ducret et al. proposed a process model which shall serve for optimizing TCAP sequences. The latter is based on material and energy balances, dividing the Pd column into equal volumes assuming continuous stirred tank reactors (CSTR), allowing for time dependent simulation of establishing process conditions and product composition of a H₂-D₂ separation scenario [104]. A simulation tool to respect a TCAP set-up of Pd column and molecular sieve was developed by Zhou et al. to investigate the impact of feed amount, reflux ratio and set-point temperatures on the separation efficiency [105]. A detailed two dimensional process model depicting axial and radial spatio-temporal evolution of temperature, pressure and composition is implemented in COMSOL by Robinson and Salloum to evaluate the effectiveness of two combined Pd beds in comparison to TCAP [70].

However, all these models simulate only absorption columns exploiting palladium hydride formation and the simulation of TCAP. In contrast to that, to the best of the authors knowledge, the presented CMH-TSA model developed in this work is first of its kind using two different metallic absorption materials, while depicting the dynamic interaction of two active separation columns during process operation.

5.1 Model Set-up and Numerical Methods

The CMH-TSA model is implemented in the Aspen Custom Modeler flow sheet simulation software using one dimensional (1D) transient models. It can serve either as stand-alone CMH-TSA process model or as system unit to be implemented in the overall fuel cycle simulator framework [22]. The model scope includes a column pair of namely a palladium and an titanium-manganese column which dynamically interact during processing a mixed feed of hydrogen isotopes. Those absorption columns are depicted by ideal plug flow reactor models. Simulation results deliver predictions for establishing transient process pressures, transient temperatures and compositions profiles in each column. Hence the transient product compositions from each column are determined.

To depict the occurring phenomena during the repeated process steps (c.f. Tab. 2.1) the absorption columns are discretized along their length axis in segments of length dx . Mass transport establishes between the solid absorption material phase, where atomic isotopes species are bounded, and the gas phase which consists of six molecular isotopologue species. The utilized model variables are shown for such a segment dx in Figure 5.1. The implemented transient equations are solved for each time step and are initialized using

an appropriate physical initial state for $t = 0$ s. The simulation termination criteria is specified by an upper time limit set by the user. For the presented results in general upper time limits between 7100 s (HESTIA simulations) and 60.000 s (IRPR simulations) were used, depending on the number of simulated cycles.

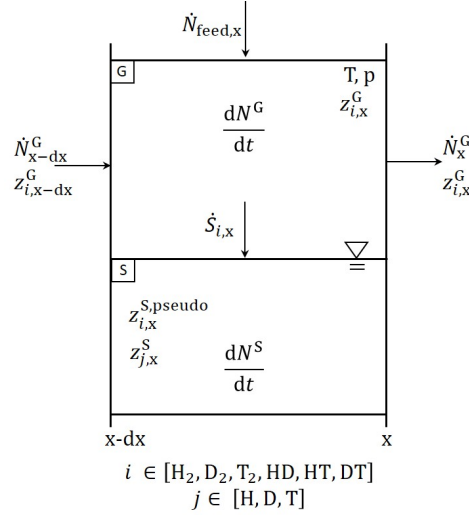


Figure 5.1: Implemented model variables and column segment dx . It is distinguished between abundance of isotope species in the gas phase (G) and solid phase (S).

To solve the models equation presented in the following standardized and pre-configured solvers provided and foreseen by the Aspen Custom Modeler software are used. For non-linear equation systems the mixed Newton method is applied, while time dependent differential balances are solved by the implicit Euler method. The relative and absolute error of $1 \cdot 10^{-5}$ serves as convergence criteria.

During simulations, the Aspen Custom Modeler dynamically adjusts the resolution of the integration time step between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-3}$ s, such that a stable solution of the results within the error tolerances is reached. The suitability of the solver pre-settings were verified for the overall fuel cycle simulator in [22] and were not optimized within the scope of this work.

5.1.1 Description of Gas Phase

The gas phase within column segment dx consists of six Q_2 isotopologue species i : H_2 , HD , D_2 , DT , T_2 and HT and shows ideal gas behavior. In addition, no tritium decay which forms He_2^3 is respected. The change of total molar amount with time $\left(\frac{\partial N^G}{\partial t}\right)_x$ of the sum of this species is impacted by the incoming and outgoing flows $\dot{N}_{x-dx}^G$ and $\dot{N}_x^G$ provided by the neighbor elements, the molar feed stream $\dot{N}_{\text{feed},x}$ and the molar flow $\dot{S}_x^G$ transferred between the gas and solid phase. The latter equals a source term if desorption takes place, i.e., Q_2 molecules emerge from the material, or a sink term if Q_2 molecules

are absorbed by the solid phase. The resulting material conservation balance for the gas inventory in column element dx is given by

$$\left(\frac{\partial N^G}{\partial t}\right)_x = \dot{N}_{x-dx}^G - \dot{N}_x^G - \dot{S}_x^G + \dot{N}_{\text{feed},x} . \quad (5.1)$$

Here, the axial transport is assumed to be purely convective, thus the axial diffusive contribution term is neglected. Analogously, the species balance for isotopologue i follows by

$$\left(\frac{\partial N_i^G}{\partial t}\right)_x = \dot{N}_{i,x-dx}^G - \dot{N}_{i,x}^G - \dot{S}_{i,x}^G + \dot{N}_{i,\text{feed},x} \quad (5.2)$$

and

$$z_{i,x}^G = \frac{N_{i,x}^G}{\sum_i N_{i,x}^G} , \quad (5.3)$$

where $z_{i,x}^G$ equals the molar isotope fraction of isotopologue i in the gas phase.

The gas transport between the columns and within a column depends on the process steps, thus demanding a depiction of multiple flow directions. While the transport between both columns during exchange and product extraction is more straightforward and one-directional, the flow conditions during feeding and internal pressure equilibration are bi-directional. To implement convective gas transport, Darcy's law is utilized. This assumption is reasonable for a Reynolds number smaller than 10, thus a laminar flow regime through the packed column. In addition, the same approach is used in [53] and [70]. Thus the pressure loss over a column segment correlates linearly to the gas velocity u and the gas viscosity $\mu(T)$

$$\left(\frac{dp}{dx}\right)_x = -\frac{\mu(T_x)}{k} u_x . \quad (5.4)$$

Replacing u by the molar flow using the ideal gas law and the column cross-section A with

$$u_x = \frac{RT_x}{p_x A} \dot{N}_x^G \quad (5.5)$$

and including a power law correlation for expressing the temperature dependence of μ

$$\mu(T_x) = \mu^* \left(\frac{T_x}{T^*}\right)^{0.668} \quad (5.6)$$

via the standard temperature T^* and standard viscosity $\mu^*(T^*)$, Eq. (5.4) can be rewritten as

$$\left(\frac{dp}{dx}\right)_x = -k_p \frac{T^{1.668}}{p_x} \dot{N}_x^G \quad (5.7)$$

with the combined transport parameter k_p

$$k_p = \frac{R\mu^*(T^*)}{kAT^{*0.668}} . \quad (5.8)$$

A first order rate approach is used to model the absorption and desorption rates represented by

$$\dot{S}_{i,x}^G = k_{\text{sorb},i}(T_x) \left(p_{i,x} - \mathbf{hys} \cdot p_{\text{eq},i,x}(z_{j,x}^S, c_x, T_x) \right) \quad (5.9)$$

using Dalton's law

$$p_{i,x} = z_{i,x}^G p_x . \quad (5.10)$$

The driving force in the kinetic expression is the difference of the partial pressure p_i of species i to the equilibrium pressure $p_{\text{eq},i,x}$. The value of $p_{\text{eq},i,x}$ is influenced by the system temperature and the amount of atomic isotopes Q absorbed in the lattice (c.f. Eq. (5.20) and Eq. (5.17)). As detailed in Subsection 2.1.2, at equal conditions $p_{\text{eq},i,x}$ varies for absorption and desorption, also known as *hysteresis* [47]. To respect this phenomenon, the *hysteresis factor* $\mathbf{hys}$ is implemented as material specific parameter which is obtained from PCI measurements. For absorption $\mathbf{hys}$ takes the value 1, such that for $p_i > p_{\text{eq},i,x}$, isotopologue species i is absorbed in the solid phase. In contrast, for desorption $\mathbf{hys}$ values smaller than 1 are implemented and desorption results for $p_i < p_{\text{eq},i,x}$. Additionally, the reaction coefficient $k_{\text{sorb},i}$ is obtained from experimental data.

Beside the hydrogenation reaction, isotope exchange reactions occur in mixed isotope gas phases. These are



For the description of the resulting equilibrium gas composition by means of the temperature dependent equilibrium constant $K_{jk,j \neq k}(T)$ of each exchange reaction, only three of these equations have to be treated, due to the linear dependency of the six reactions. Using the letters a to f as subscript for the dependent equilibrium constants the following

correlations result:

$$K_{\text{HD}} = K_{\text{a}} = K_{\text{d}} \cdot K_{\text{e}} \quad (5.12\text{a})$$

$$K_{\text{HT}} = K_{\text{b}} = K_{\text{d}} \cdot K_{\text{f}} \quad (5.12\text{b})$$

$$K_{\text{DT}} = K_{\text{c}} = K_{\text{e}} \cdot K_{\text{f}} . \quad (5.12\text{c})$$

Peters gives a correlation for the temperature dependent equilibrium constant $K_{jk,j \neq k}(T)$ for each exchange reaction based on data provided by Jones [106, 107, 108, 109]:

$$K_{jk,j \neq k,x} = A_{jk,j \neq k} \cdot \exp\left(-\frac{B_{jk,j \neq k}}{T_x}\right) . \quad (5.13)$$

The correlation parameters $A_{jk,j \neq k}$ and $B_{jk,j \neq k}$ vary for different temperature regimes. The relevant temperature range for CMH-TSA application (above 250 K) requires the parameter sets given in Table 5.1.

Table 5.1: Correlation parameters $A_{jk,j \neq k}$ and $B_{jk,j \neq k}$ to calculate equilibrium constant $K_{jk,j \neq k}(T)$ reported by Peters for isotope exchange reaction in the relevant temperature range for CMH-TSA application (above 250 K) [106].

Exchange reaction	$A_{jk,j \neq k} / -$	$B_{jk,j \neq k} / \text{K}$
$\text{H}_2 + \text{D}_2 \rightleftharpoons 2 \text{HD}$	4.075	19.456
$\text{D}_2 + \text{T}_2 \rightleftharpoons 2 \text{DT}$	4.518	166.588
$\text{H}_2 + \text{T}_2 \rightleftharpoons 2 \text{HT}$	4.207	75.316

However, the timescale of reaching chemical equilibrium due to equilibration reactions between the isotopologues given in Eq. (5.11) equals months [110], thus the CMH-TSA process timescales of minutes are distinctly shorter. Therefore, the presented equilibration reactions are neglected in Eq. 5.2 for modelling the gas phase composition. Instead, they are the base for modelling the composition of isotopes emerging from the metal lattices during desorption. This approach is explained further in the following section.

5.1.2 Description of Solid Phase

To model the repeated uptake and desorption of molecular hydrogen isotopes, the absorption materials are regarded as cycling stable with clean surface and completed activation. No degradation, i.e, loss of reversible capacity, no decrepitation, i.e., self-pulverization during hydrogenation, and no disproportionation, i.e., local change of alloy composition,

over the process time are considered. In Eq. (2.1) the underlying reaction during metal hydride formation is given. The key challenge of the presented CMH-TSA model is to link a gas phase consisting of six molecular isotopologues to a solid phase with only the three atomic species H, D and T. The sum of all absorbed Q species N^S depends on the source term $\dot{S}_x^G$ according to

$$\left(\frac{dN^S}{dt} \right)_x = \dot{S}_x^G, \quad (5.14)$$

where $N^S = \sum_j N_j^S$.

The species balance follows by

$$\left(\frac{dN_j^S}{dt} \right)_x = 2\dot{S}_{jj,x}^G + \dot{S}_{jk,j \neq k,x}^G + \dot{S}_{jl,j \neq l,x}^G, \quad (5.15)$$

respecting the dissociation of two-atomic molecules into atoms ($j,k,l = \text{H, D and T}$) when being absorbed in the lattice and with

$$z_{j,x}^S = \frac{N_{j,x}^S}{\sum_j N_{j,x}^S} \quad (5.16)$$

representing the atomic composition of the solid phase. The total molar amount of absorbed species Q in relation to the molar amount of absorbents N_{mat} is defined as *concentration* c and a figure of merit of the loading of the metal lattice

$$c_x = \frac{N_x^S}{N_{\text{mat},x}}. \quad (5.17)$$

The metal surface, where molecular species first absorb and immediately dissociate in two atoms and similarly atomic species recombine and desorb as molecular isotopologues into the surrounding gas phase, is modelled by an interface phase. This *pseudo-interface* is composed of molecular Q_2 species (thus comparable to the gas phase) and influenced by the exchange with the gas phase (absorption) and the recombination of the atoms emerging from the solid phase (desorption). The composition of the pseudo-interface is a representative molecular composition of the atomic composition of the solid phase valid for the system temperature and loading in the lattice. To connect the atomic composition z_j^S of species Q to the molecular composition $z_i^{S,\text{pseudo}}$ of homo- and hetero-isotopologue species i , an atomic balance is utilized:

$$z_{j,x}^S = 2z_{jj,x}^{S,\text{pseudo}} + z_{jk,j \neq k,x}^{S,\text{pseudo}} + z_{jl,j \neq l,x}^{S,\text{pseudo}}. \quad (5.18)$$

The composition of the emerging isotopologue stream is assumed to equal the equilibrium composition of the isotope exchange reaction given in Eq. (5.11) for the respective system

temperature. The underlying temperature dependent equilibrium constant $K_{jk,j \neq k}(T_x)$ follows

$$K_{jk,j \neq k}(T_x) = \frac{z_{jj,x}^{S,pseudo} \cdot z_{kk,x}^{S,pseudo}}{(z_{jk,j \neq k,x}^{S,pseudo})^2} . \quad (5.19)$$

The respective correlation for $K_{jk,j \neq k}$ is given in Table 5.1. The hypothesis of equilibrium composition is reasonable, since the metal acts as catalyst for the isotopic exchange reaction and thus accelerate the equilibrium reaction. A comparable approach was exploited in [53].

To correlate the species specific equilibrium pressure $p_{eq,i}$ to the abundance of isotopologue i in the lattice as required for Eq. (5.9), Raoult's law is used. In general, Raoult's law is valid for ideal mixtures. Then, the establishing partial vapor pressures of component i in a closed gas-liquid-equilibrium follow from the molar abundance of i in the liquid multiplied by the vapor pressure of the pure component i . This approach is transferred to the metal-hydride system, thus an interacting gas-solid phase. As Raoult's law is suitable for mixtures in which species have an almost similar molecule structure (for example benzene and toluene) [111], it is assumed that the establishing structures of a metal protide, metal deuteride and metal tritide fulfil this requirement. Also Wicke and Nernst utilized this approach for the estimation of establishing mixed isotope equilibrium pressures of the H-D-Pd-system [73].

Thus, the species specific equilibrium pressure $p_{eq,i}$ follow from

$$p_{eq,i,x} = z_{i,x}^{S,pseudo} p_{eq,pseudo,i,x} (z_i^{S,pseudo} = 1, c_x, T_x) , \quad (5.20)$$

where $p_{eq,pseudo,i}(c_x, T_x)$ refers to the establishing pseudo-equilibrium pressure if only species i was present in the solid phase. The value of homo pseudo-equilibrium pressure follows from experimental PCI data for different isotope species and temperatures (c.f. Sec. 5.2.1).

5.1.3 Energy Balance

The system energy within column segment dx follows from the balance

$$\left(\frac{dH}{dt} \right)_x = \dot{H}_{x-dx} - \dot{H}_x + \dot{Q}_x + \dot{H}_{r,x} , \quad (5.21)$$

where $\dot{H}_{x-dx}$ and $\dot{H}_x$ equal the convective heat transfer provided by the neighbor elements and $\dot{Q}_x$ reflects the radial heat transfer given by a connected heating system. $\dot{H}_{r,x}$ is the released energy during exothermic hydride formation within dx . The model complexity can be reduced by neglecting the convective terms, assuming that the heat input by the heating system is dominant ($\dot{Q}_x \gg \dot{H}_{x-dx}, \dot{H}_x$). Additionally, the thermal conductivity

of the bed, i.e., the heat transfer between the particles, is neglected. The solid phase is considered to dominate the integral systems heat capacity and density, thus these structure and absorption material characteristics are summarized in c_p^S and ρ^S . The former assumes independence of the degree of hydration which means $c_{p,\text{metal}} = c_{p,\text{metal hydride}}$.

These simplifications lead to a homogenous temperature in column segment dx ($T_{\text{gas},x} = T_{\text{mat},x}$) such that Eq. (5.21) can be rewritten to

$$\left(\frac{dT}{dt}\right)_x = \frac{1}{\rho^S dx c_p^S} (\dot{Q}_x + \Delta h_{\text{sorb}} \dot{S}_{i,x}^G) , \quad (5.22)$$

where Δh_{sorb} is the heat of absorption released during hydride formation. The thermal kinetic approach follows from

$$\dot{Q}_x = k_{\text{heat}} \pi D_{\text{col}} dx (T_{\text{oil}} - T_x) , \quad (5.23)$$

where the driving force is given by the temperature difference between column segment temperature T_x and the temperature of the heating media T_{oil} provided by the external heating source. k_{heat} is the heat transmittance coefficient between the heating media and the wall of the column to the absorption material for a column of diameter D_{col} . Ideal energy supply is assumed such that no temperature variations over a process step time and the complete columns length establish, meaning

$$\frac{dT_{\text{oil}}}{dt} = \frac{dT_{\text{oil}}}{dx} = 0 . \quad (5.24)$$

5.1.4 Boundary Conditions

The columns, the transfer and extraction piping and the heating and cooling system are considered to be adiabatic to the environment. In addition, no hydrogen permeation through the structural material is assumed. The mass transfer between the modelled columns and across the systems border is implemented by physical matter flows which have properties including pressure, temperature and molar composition. All process cycling steps are monitored and controlled by time-triggered valve models. The process times used for the different process steps are based on preliminary tests in HESTIA and process times reported in literature [35, 57] to control the valve positions. Two kind of valve models are implemented to govern the process flows.

The flows across the feed valve and the product extraction valves are set by a mass flow controller in a technical TSA set-up. Accordingly, a **fixed value** is set as boundary flow condition, representing an open valve. If the valve is closed during the respective process

step, the set-point is 0 mol/s such that no flow is allowed to cross the system border

$$\dot{N}^G = \begin{cases} 0, & \text{Closed valve,} \\ \text{fixed value,} & \text{Open valve .} \end{cases} \quad (5.25)$$

In contrast to these valves, which control one-directional flows, the exchange valve between the absorption columns allows for flows in both directions, depending on the pressure difference between both columns. The establishing flow is correlated linearly to this pressure difference $p_{C1} - p_{C2}$ using a flow coefficient k_{CV} for an open valve

$$\dot{N}^G = \begin{cases} 0, & \text{Closed valve,} \\ k_{CV} (p_{C1} - p_{C2}), & \text{Open valve .} \end{cases} \quad (5.26)$$

Depending on the resulting sign, the flow direction is defined. This is comparable to representation of flows occurring during internal column pressure equilibration.

Beside the flow boundary conditions the temperature swings are implemented by defined set-point temperatures T_{oil} . For each column an absorption temperature T_{cold} and a desorption temperature T_{hot} is chosen and serves as driving force for Eq. (5.23). The switch between those is time-triggered similarly to the valve positions.

$$T_{oil} = \begin{cases} T_{hot}, & \text{Heating,} \\ T_{cold}, & \text{Cooling.} \end{cases} \quad (5.27)$$

The time-controlled switch between the presented boundary values allows for implementation of various process steps and operation scenarios to investigate suitable repeating CMH-TSA process cycles. Influences on the separation efficiency for different process temperatures and exchange times can be flexibly adapted and compared.

5.1.5 Extrapolation to Tritium Operation

To evaluate CMH-TSA technology for the IRPR system, the model has to enable CMH-TSA simulation under tritium operation. This requires an extrapolation of metal-hydrogen-characteristics observed from protium and deuterium experiments to tritium-metal-systems. Therefore, the correlations for modelling the equilibrium pressures p_{eq,T_2} , $p_{eq,DT}$ and $p_{eq,HT}$ are required. They are implemented by Eq. (5.20) and (5.31), similar to the non-tritiated species. As observed from evaluation of PCI data in Table 5.2, the slopes of each linear function representing the $\alpha - \beta$ - and β -phase are independent from the isotopologue species. However, the concentration at which the transition of $\alpha - \beta$ - to β -phase occurs

is affected by the type of isotopologue, therefore, the extrapolation is realized there.

As known from literature, the isotope effect between protium and deuterium species is greater than between deuterium and tritium species, i.e., $\alpha_{HD} > \alpha_{DT}$ [48, 51, 73]. A correlation is required to extrapolate a species i related quantity ξ_i , for example the equilibrium pressure, from measured values ξ_{H_2} and ξ_{D_2} to ξ_{T_2} . To do so, it is assumed, that $\frac{\alpha_{DT}}{\alpha_{HD}}$ is constant over the relevant temperature range, i.e.,

$$\frac{|\xi_{D_2} - \xi_{T_2}|}{|\xi_{H_2} - \xi_{D_2}|} = \text{const.} \quad (5.28)$$

To calculate ξ_{T_2} , the absolute difference $|\xi_{H_2} - \xi_{D_2}|$ is weighted by the square root of the ratio of the molar masses of D_2 over T_2 which follows from the zero-point energy consideration and thus the vibrational energies for a harmonic oscillator (c.f. Subsec. 2.1.3). An isotope dependent quantity ξ_{T_2} follows from

$$\xi_{T_2} = \xi_{D_2} \pm |\xi_{D_2} - \xi_{T_2}| = \xi_{D_2} \pm \left(|\xi_{H_2} - \xi_{D_2}| \cdot \sqrt{\frac{\tilde{M}_{D_2}}{\tilde{M}_{T_2}}} \right) \quad (5.29)$$

To extrapolate a known deuterium quantity ξ_{D_2} to the corresponding tritium quantity ξ_{T_2} , the direction of the isotope effect specifies if the second part in the equation is added or subtracted. For a normal isotope effect, thus $\xi_{T_2} > \xi_{D_2} > \xi_{H_2}$, the difference between both quantities, i.e., $|\xi_{D_2} - \xi_{T_2}|$, is added. In turn, for an inverse isotope effect $|\xi_{D_2} - \xi_{T_2}|$ is subtracted demanding for the absolute value in Eq. (5.29), since $\xi_{D_2} > \xi_{H_2}$.

To verify the given extrapolation approach, the reported desorption equilibrium pressures for the Pd-T system by Lässer of tritium are estimated by the reported data of the corresponding Pd-D and Pd-H system [51]. For $\xi_i = p_{eq,i}$, the measured and extrapolated data is compared in Figure 5.2.

The extrapolated tritium equilibrium values differ up to 20 % from the experimental data for $T = 273 \text{ K}$. Nevertheless, the extrapolated values are comparable enough for a first approach, considering the simplification of temperature independence.

In contrast to this approach, Robinson and Salloum incorporate isotope effects on diffusion, lattice expansion, equilibrium pressure and so on in their COMSOL model to differ between the isotope effects of a metal-hydrogen-system [70]. These approaches would highly increase the computational effort and model complexity. Simpler ratios like the simple square root implementation lead to larger inaccuracy to the experimental data. Finally, all simulated CMH-TSA results need to be verified by tritium experiments to supporting the versatility of CMH-TSA technology. However, first, simulations shall support the utility of the process before performing separation experiments using tritium, which requires complex infrastructure.

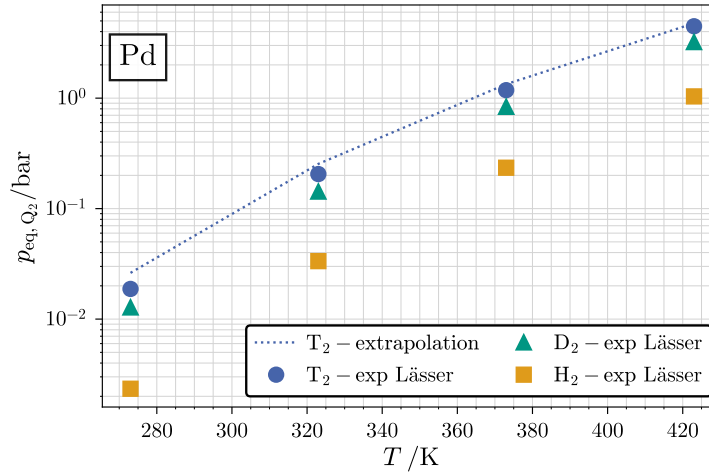


Figure 5.2: Verification of utilized extrapolation approach to estimate tritium equilibrium pressures on the base of deuterium and protium data. Data for comparison derived by [51].

5.2 Derivation of Model Parameters and Sub-model Validation

Experimental data obtained from studies performed in MAIA and HESTIA allow for determination of required model parameters to calculate establishing equilibrium pressures, absorption and desorption kinetics and flow characteristics. In the following, the applied methods to derive those respective parameter values are presented and the sub-models validated.

5.2.1 Implementation of Equilibrium Pressure

Eq. (5.20) demands the implementation of establishing equilibrium pressures $p_{\text{eq,pseudo},jj}$ occurring in a homo-isotopologue-material system. This is realized by splitting the homo-isotopologue PCI in two connected correlations, representing the occurring phases of an ideal PCI (c.f. Fig. 2.1). For low hydrogen loadings in the α -Phase up to the limit of $c_{\alpha\text{pha}}$, which defines the transition between α and $\alpha - \beta$ -phase and depends on the absorption material, Sieverts' law is used

$$c = K_{\text{SV},jj} \sqrt{p_{\text{eq,pseudo},jj}}, \quad 0 < c < c_{\alpha\text{pha}}, \quad (5.30)$$

where $K_{\text{SV},jj}$ is the Sieverts' constant for homo-isotopologue absorption.

The $\alpha - \beta$ - and β -phase is implemented using a *hinge-function*. This function allows for a continuously differentiable description of two intersecting linear functions. By linear regression of both regimes, i.e., plateau- ($= 1$) and β -phase ($= 2$), the hinge-function enables a continuous correlation of equilibrium pressure and concentration. Utilized model

parameters of this hinge-function are the slopes m_1 and m_2 of each individual linear function, the intersect ($= ic$) and a smoothing factor δ , which adapts the intersection angle. A schematic plot of the utilized fit-combination, its parameters and their derivation by PCI data is shown in Figure 5.3.

The complete correlation of $p_{eq,pseudo,jj}$ is written as

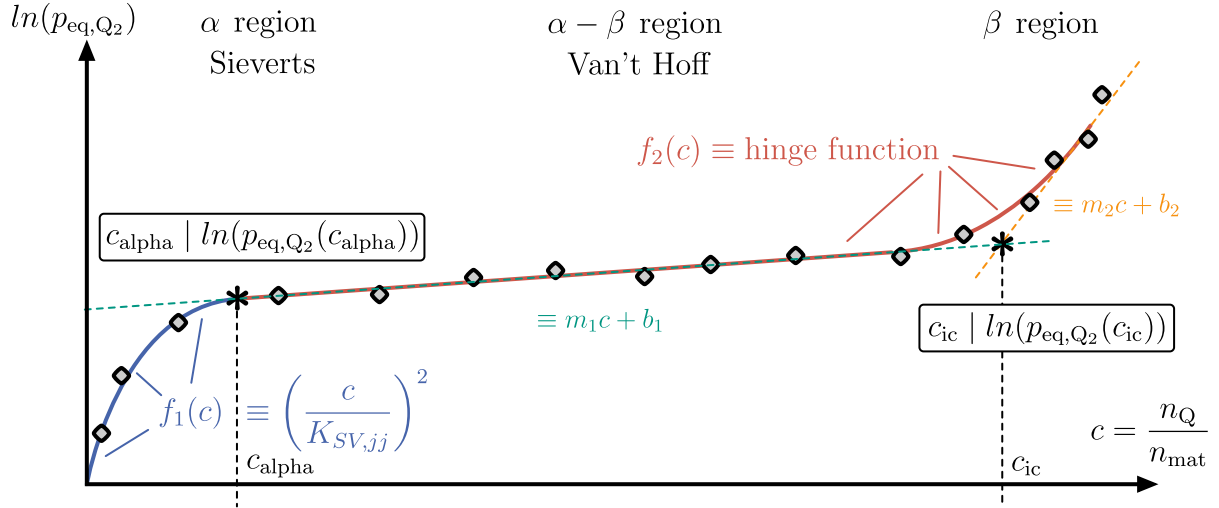


Figure 5.3: Schematic depiction of the implemented correlation to calculate isotope, temperature and loading dependent equilibrium pressures. To determine the correlation parameters, homo-isotopologue pressure-concentration-isotherm measurements are required. Within the plateau- and β -region a continuous "hinge-function" $f_2(c)$ is implemented, while Sieverts' law $f_1(c)$ is applied to model the establishing equilibrium pressures in the α -phase. Correlation parameters are described in the text.

$$p_{eq,pseudo,jj} = \begin{cases} \left(\frac{c}{K_{SV,jj}} \right)^2, & 0 < c < c_{\alpha}, \\ \exp \left\{ \ln(p_{ic,jj}) + m_1(c - c_{ic,jj}) + (m_2 - m_1)\delta \ln \left(1 + \exp \left(\frac{c - c_{ic,jj}}{\delta} \right) \right) \right\}, & c > c_{\alpha}. \end{cases} \quad (5.31)$$

The transition point between Sieverts' regime and hinge-function is defined by the concentration c_{α} as mentioned above. Here, further absorption of hydrogen results in nucleation of a metal hydride phase (β -phase, c.f. Subsec. 2.1.2). Depending on the value of c either the upper case ($c < c_{\alpha}$) is used to calculate the resulting equilibrium pressure or the lower case ($c > c_{\alpha}$).

For the upper case, $K_{SV,jj}$ is determined from c_{α} while the resulting value of $p_{eq,pseudo,jj}(c_{\alpha})$ obtained by the linear function representing the $\alpha - \beta$ -regime ($=1$)

$$K_{SV,jj} = \sqrt{\frac{c_{\alpha}^2}{p_{eq,pseudo,jj}(c_{\alpha})}} = \sqrt{\frac{c_{\alpha}^2}{\exp \{ m_{1,jj} \cdot c_{\alpha} + b_{1,jj} \}}} \quad (5.32)$$

For the lower case, the parameters coordinates of the intersect, i.e., $\ln(p_{ic})$ and c_{ic} , the smoothing factor δ and the slopes m_1 and m_2 are required. The temperature dependent coordinates of the intersects are calculated from the parameters of both linear regressions for each homo-isotopologue species respectively. Hence, the concentration c_{ic} at the intersection follows from

$$c_{ic,jj} = \frac{b_{2,jj} - b_{1,jj}}{m_{1,jj} - m_{2,jj}} , \quad (5.33)$$

where $b_{1,jj}$ and $b_{2,jj}$ are the intersections of the linear fit functions of the α - β - and β -phase. The corresponding logarithmic equilibrium pressure $\ln(p_{ic,jj})$ follows from the individual linear functions of the β -phase-regime

$$\ln(p_{ic,jj}) = m_{2,jj} \cdot c_{ic,jj} + b_{2,jj} . \quad (5.34)$$

The parameters for the presented correlation are derived from PCI measurements using H_2 , D_2 , Pd and $TiMn_{1.5,mod}$ performed in MAIA (Pd) and the commercial Sieverts' apparatus *GasPro HA* ($TiMn_{1.5,mod}$). The obtained data is fitted linear and the resulting parameters correlated to the temperature and isotope species respectively. The implemented correlations for each model parameter and absorption material are summarized in Table 5.2. It should be noted, that for other absorption materials different temperature and isotope dependencies of the model parameters may be observed. From the data investigations, the following conclusions concerning the parameter dependence of system temperature and isotope species were drawn:

- For both absorption materials the sloping of the plateau-pressure is independent of temperature and isotope species.
- The transition from plateau- to β -phase is temperature and isotope dependent for both materials.
- While the pressure increase triggered by further absorption (increasing c) appears to be independent of temperature and isotope species for palladium, in the case of $TiMn_{1.5,mod}$ it is temperature dependent. This is concluded from varying steepnesses of the PCIs in the β -region.
- For both absorption materials, all analysed temperatures and isotopes a smoothing factor $\delta = 8 \cdot 10^{-4}$ was determined.

In a CMH-TSA process absorption materials interact with multi-isotopologue gas phases. To model the resulting system pressures, the pseudo-equilibrium pressures $p_{eq,pseudo,jk}$ for mixed isotopologue species are implemented using the mean of both homo-isotopic

Table 5.2: Implemented model parameters for hinge-function utilized to calculate the establishing equilibrium pressure in the plateau and β -region based on PCI measurements for Pd and $\text{TiMn}_{1.5,\text{mod}}$ dependent on the temperature and homo-isotopologue species.

	Palladium	$\text{TiMn}_{1.5,\text{mod}}$
m_1	1.858	2.534
$j = \text{H}$	$0.026 \cdot T - 4.766$	$0.053 \cdot T - 10.237$
$b_{1,jj} \quad j = \text{D}$	$0.030 \cdot T - 4.713$	$0.057 \cdot T - 11.704$
$j = \text{T}$	$0.033 \cdot T - 4.670$	$0.060 \cdot T - 12.902$
m_2	44.036	$-0.317 \cdot T + 115.494$
$j = \text{H}$	$0.037 \cdot T - 34.327$	$0.281 \cdot T - 90.947$
$b_{2,jj} \quad j = \text{D}$	$0.031 \cdot T - 30.477$	$0.276 \cdot T - 89.970$
$j = \text{T}$	$0.026 \cdot T - 27.333$	$0.272 \cdot T - 89.171$
δ	$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$

pseudo-equilibrium pressures $p_{\text{eq,pseudo},jj}(c, T)$ and $p_{\text{eq,pseudo},kk}(c, T)$ according to

$$p_{\text{eq,pseudo},jk}(c, T) = \frac{p_{\text{eq,pseudo},jj}(c, T) + p_{\text{eq,pseudo},kk}(c, T)}{2} . \quad (5.35)$$

To validate the presented implementation of the establishing equilibrium pressures, PCIs of Pd (0.024 mol) were measured in MAIA for three process relevant temperatures using an isotopic mixture of 50 % H_2 and 50 % D_2 . In addition, a room temperature PCI was investigated for $\text{TiMn}_{1.5,\text{mod}}$ (0.121 mol), as higher system temperatures are out of the pressure range operable in MAIA. The obtained experimental data and estimated equilibrium pressures by the model are compared in Figure 5.4.

The resulting equilibrium pressure for HD-hetero-isotopologues for Pd are represented well by the utilized model approach in the process relevant region (plateau and beta region), differing by 12.2 % maximum for room temperature and 50 °C and 38.9 % at 100 °C. Also the transition between the phases, which shifts to lower concentrations for higher system temperatures is represented by the utilized correlations. However, establishing pressures within the α -phase are overestimated up to factor 4. Since the CMH-TSA process is operated within the plateau- and β -region, the reduced model accuracy is accepted. Comparing the calculated PCI of $\text{TiMn}_{1.5,\text{mod}}$ to the experimental results, the modelled plateau-pressures deviate by 19.3 % maximum and the reachable concentration in the β -phase are underestimated by 11.6 %. While the hinge-function parameters were adapted to PCI measurements of the commercial Sieverts' apparatus (c.f. Subsec. 3.2.4), as it provides the capability to measure at system temperatures below room temperature, the hetero-isotopologue PCI was obtained from MAIA. The observed increased plateau-capacity may

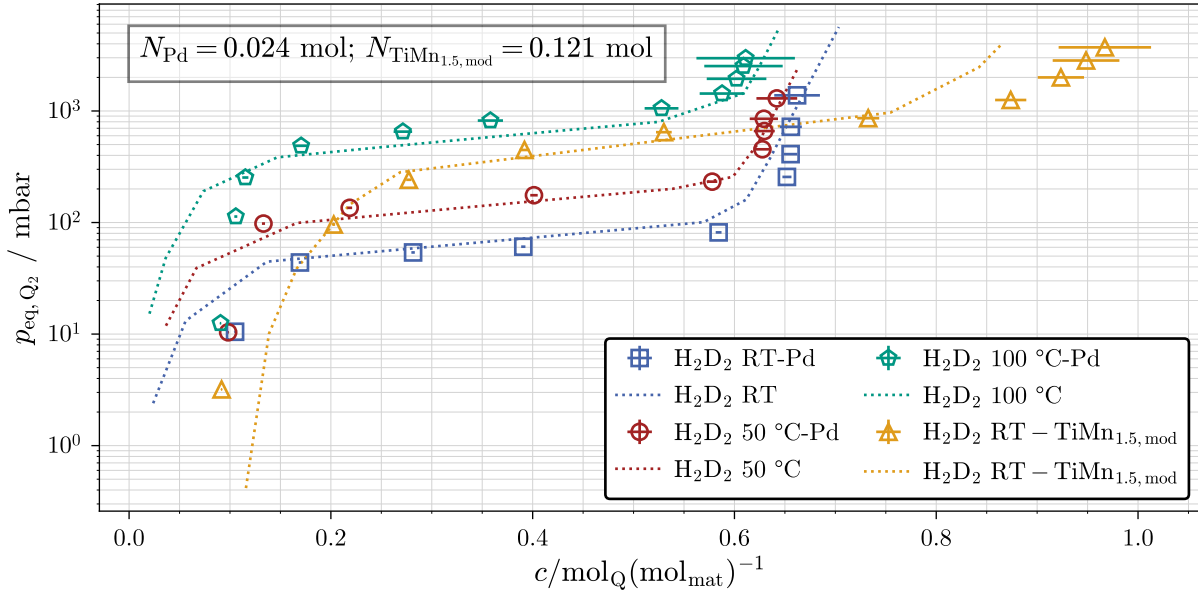


Figure 5.4: Comparison of experimental PCI data for several system temperatures exposing $\text{TiMn}_{1.5,\text{mod}}$ and Pd to an equimolar $\text{H}_2\text{-D}_2$ -gas phase. Error bars calculated according Type B uncertainty estimation using sensor uncertainties (c.f. Tab. B.1).

be caused by an additional bake-out treatment of the $\text{TiMn}_{1.5,\text{mod}}$ sample investigated in MAIA, leading to lower residual hydrogen amounts in the metal lattice in comparison to the 30 min evacuation procedure applied between the repeated PCI measurements in the commercial Sieverts' apparatus. Thus, the definition of $c = 0 \text{ mol}_Q/\text{mol}_{\text{TiMn}_{1.5,\text{mod}}}$ is shifted between both apparatus.

5.2.2 Validation of Sorption Kinetics

A dedicated 0D absorption model is utilized to validate the kinetic approach (c.f. Eq. (5.9)) implemented in the presented CMH-TSA model. All balances used to describe the occurring gas-solid-phase interactions are similar to the equations given in Section 5.1. This reduced model allows for accessing the implemented approach of linking absorption equilibrium and kinetics independently of gas transport and heat input influences. To do so, the pressure evolution in the gas phase is calculated for a given feed stream, material amount, system volume and temperature and compared to experimental data obtained from corresponding MAIA experiments. In those studies dynamic PCI were measured at room temperature, thus Pd (0.024 mol) and $\text{TiMn}_{1.5,\text{mod}}$ (0.121 mol) were charged with continuous feed streams of H_2 and an equimolar $\text{H}_2\text{-D}_2$ -mixture while recording the pressure increase. A flow sheet of the described procedure is given in Figure 5.6.

To determine the reaction coefficient k_{sorb} , the parameter value was varied between $1 \cdot 10^{-2}$ and $5 \cdot 10^{-10} \text{ mol}/(\text{sPa})$. Simulated pressure profiles using $5 \cdot 10^{-6} \text{ mol}/(\text{sPa})$ were found to

most accurately resemble the experimental data and are shown in Figure 5.5 for different feed flows and materials.

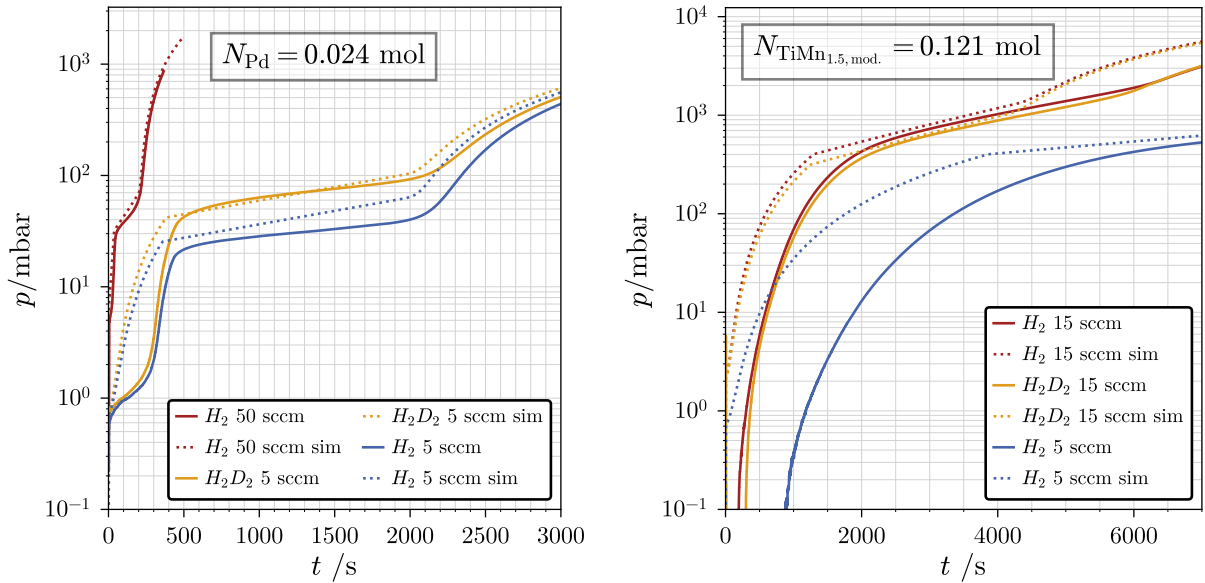


Figure 5.5: Dynamic pressure-concentration-isotherms obtained experimental (solid lines) and simulated (dashed lines) for various feed streams (5, 15 and 50 sccm (= standard cubic centimetres)) and compositions (H_2 and equimolar $\text{H}_2\text{-D}_2$ gas mixture) at room temperature charging palladium (left) and $\text{TiMn}_{1.5,\text{mod}}$ (right). Error bars are smaller than the lines.

For the Pd-system, the course of the pressure evolution is represented well by the simulated profiles. However, for H_2 charging the plateau-pressure differ from 21.5 to 59.5 %, thus the plateau-sloping is overestimated by the simulation. In contrast to that, for the $\text{H}_2\text{-D}_2$ -mixture the deviation is only 3.3 %. In the β -region differences up to 20 % occur for all investigated feed rates. As observed for the simulated equilibrium pressures described in Subsection 5.2.1, the establishing pressure in the α -phase is overestimated. Nevertheless, since the operation range of CMH-TSA is the plateau- and β -region, this is accepted, such that the accurate representation of the transition between α - and plateau-region is of higher interest, which is underestimated by 18.7 %. Instead, the transition between plateau- and β -region only differs by 4.7 % maximum.

The transition of α - to plateau-region extends over a larger experimental time for the $\text{TiMn}_{1.5,\text{mod}}$ -system in contrast to Pd. All establishing pressures for the various feed flow rates are overestimated by the corresponding simulation. In the plateau-region deviations of 6.7 to 14.7 % occur. The transition from plateau- to β -region is underestimated, which might be caused from the extended absorption capacity observed in MAIA, as described for the equilibrium pressure simulation in Subsection 5.2.1.

In general, reaction coefficients are dependent of the system temperature. This is neglected for the determined k_{sorb} , as the heating and cooling kinetics are rate determining (absorption rates $\gg$ heating rates) [103] which is why the above described deviations are tolerated. A similar approach of temperature independent reaction coefficients was exploited in [70]. However, beside the temperature also the material amount impacts the absorption kinetics. A review by Jensen et al. of hydrogen storage material properties in regard to scale-up of hydrogen storage tanks reports of impact of the material amount towards kinetics and transport characteristics in comparison to lab scale evaluations [112]. It states that higher material amounts may reduce obtained lab scale kinetics, which is why industrial scales should be revised accordingly. Therefore, it is strongly suggested to validate absorption kinetics for a relevant process scale in future and optimize the kinetic model, if proven to be necessary.

5.2.3 Implementation of Flow Parameter

For the determination of the flow coefficient k_p applied in the transport equation Eq. (5.7), flow experiments were performed in HESTIA. For this, the absorbent Pd was perfused at various temperatures using H_2 and different feed streams. After reaching a steady state in metal hydride formation, i.e., saturation of the lattice at the respective experimental temperature, the pressure drop over the Pd columns length was measured. The schematic experimental set-up is shown in Figure 5.7. Since the Darcy equation is only valid for incremental pressure drops, but differences of about 20% were observed over the bed length, the well known correction for elongated beds of L_{col} proposed by Santomaso et al. was used to determine k_p

$$\left(\frac{p_{\text{in}} - p_{\text{out}}}{L_{\text{col}}} \right)_{\text{corr}} = \frac{p_{\text{in}}^2 - p_{\text{out}}^2}{2p_{\text{in}}L_{\text{col}}} , \quad (5.36)$$

where p_{in} is equals the pressure at the column inlet and p_{out} is the pressure at the column outlet [113]. To calculate k_p , Eq. (5.7) is extended by Eq. (5.36) and rearranged to

$$p_{\text{in}} \left(\frac{p_{\text{in}}^2 - p_{\text{out}}^2}{2p_{\text{in}}L_{\text{col}}} \right) = k_p T^{1.668} \dot{N}^G . \quad (5.37)$$

Measuring the pressure drops for varying flows at room temperature, the obtained linear function shown in Figure 5.8 allows for calculating k_p from the respective slope divided by $T_{\text{RT}}^{1.668}$. Utilizing the hydrogen standard viscosity of $\mu_{\text{H}_2}(293\text{K}) = 8.8 \cdot 10^{-6} \text{ Pas}$ as reported by the NIST database, this leads to a value of $k_p = 3.5\text{e}^7 \text{ sPa}^2\text{K}^{-1.668}\text{mol}^{-1}\text{m}^{-1}$ [114].

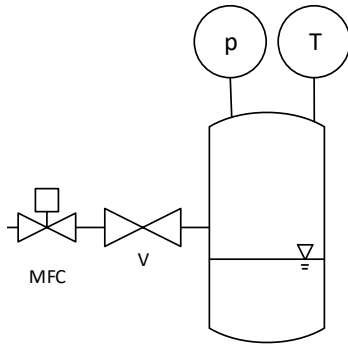


Figure 5.6: Schematic experimental procedure to measure dynamic PCIs.

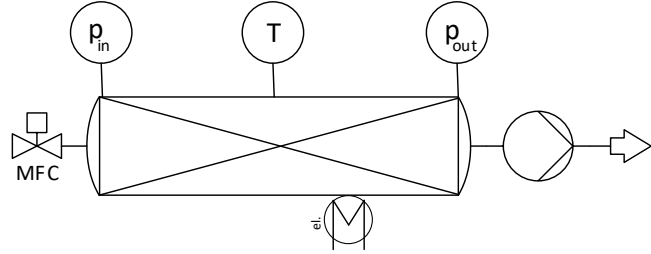


Figure 5.7: Schematic experimental procedure to obtain transport coefficient k_p by flow through experiments using the Pd column of the set-up HESTIA.

Using this transport coefficient, the pressure drops for temperatures of 50 and 100 °C were calculated by the transport model and compared to experimental data, which is also shown in Figure 5.8.

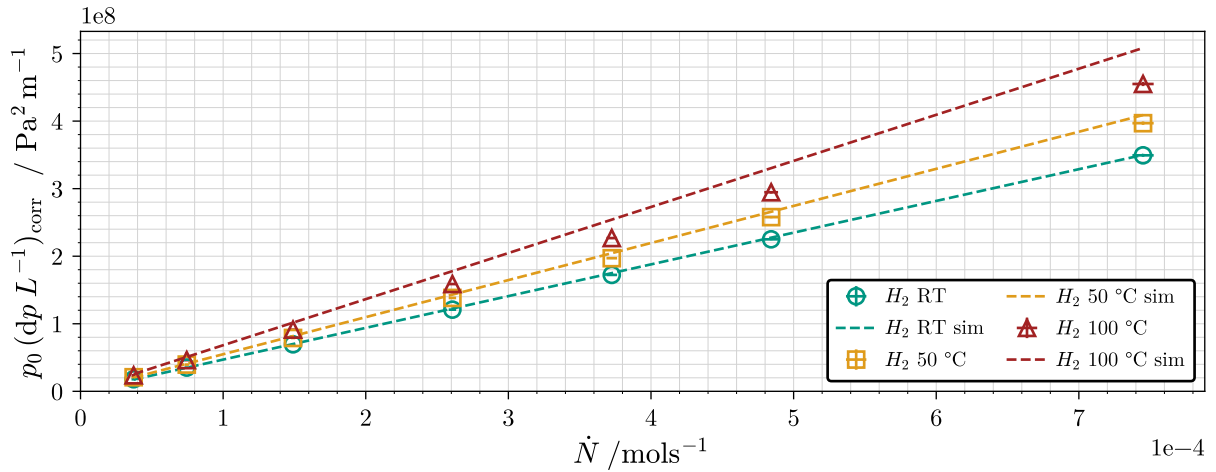


Figure 5.8: Pressure drops obtained from measurements and estimated by transport model equation for room temperature, 50 and 100 °C using H_2 and various flows. Error bars represent standard deviation of five repetitions.

A good agreement between experiment and simulation is observed and are typically in the range of 1 to 1.5 % for room temperature. For higher temperature the deviation increases for increasing molar flows. However, the highest difference is around 12 % for 100 °C and therefore in a tolerable range.

5.3 Simulation of HESTIA Experiments

To validate the model concerning its capability to mimic CMH-TSA process conditions, i.e., resulting temperatures, pressures, and the reachable separation efficiency, HESTIA separation experiments are simulated, which were presented in Section 4.3 and 4.4. Not only the experimental results of single column and coupled columns studies shall be displayable by the simulations, in addition they shall support the assumptions concerning the state of the $\text{TiMn}_{1.5,\text{mod}}$ alloy filled into the column (c.f. Sec. 4.5). First, the simulation procedure to mimic HESTIA experiments is described in Subsection 5.3.1 and the grid impact is discussed. Then the simulated data of each mimicked HESTIA experiment is set into comparison to the corresponding measured operational temperatures, pressures and product compositions.

5.3.1 Procedure and Study of Grid Impact

All utilized parameters, e.g. geometry parameters and further material parameters, and initialisation values are given in Table C.1 and C.2 in the appendix for each simulation case.

While a HESTIA experiment starts with feeding a hydrogen mixture to the Pd column, the simulation is initialized by a completed exchange phase, where Pd is in absorption and $\text{TiMn}_{1.5,\text{mod}}$ in desorption phase. Then the temperatures are switched and the cycling repeated for a given simulation time. These different initial states have to be brought into agreement. Furthermore, while the sampling in HESTIA is pressure driven, the model requires a definition of an extraction flow stream. The composition of isotopes of this stream is monitored over time. The described automatization routine given in Table 5.3 summarizes the process step times, the valve settings and temperature boundary conditions.

To compare similar hydrogen inventories, the total hydrogen amount of the experiment is calculated. Then the pressure during exchange from $\text{TiMn}_{1.5,\text{mod}}$ to Pd is determined. The absorption temperature of Pd is used for initializing the Pd column. The concentration is chosen in the β -region while adapting the pressure to obtained experimental values. On the other side, the TiMn column is initialized in desorption phase, thus temperature and a concentration values reflecting the plateau-region at low concentrations. The values for c_{Pd} , c_{TiMn} and the initial pressures of both columns are iterated until the sum of both hydrogen inventories in the column satisfy $N_{\text{tot,Pd}} + N_{\text{tot,TiMn}} = N_{\text{tot,exp}}$. The composition of isotopes in both columns are initialized using an equimolar composition in solid and gas phase, i.e., $z_{\text{H}_2}^{\text{G}} = z_{\text{D}_2}^{\text{G}}$ and $z_{\text{H}}^{\text{S}} = z_{\text{D}}^{\text{S}}$. During sampling, the extraction valve model is utilized and a fixed extraction stream defined (c.f. Eq. (5.25)) to withdraw a sample amount similar to the experiment (c.f. Tab. 4.2 and 4.3). In pre-investigations the

Table 5.3: Automated process step routine to mimic HESTIA operation.

Step	V – Exch	V – Pd	V – TiMn	V – Feed	T _{Pd}	T _{TiMn}	Time
1	X	X	X	X	cold	hot	$t_{\text{init}} = 0$
2	X	X	X	X	hot	cold	t_{heat}
3	O	X	X	X	hot	cold	t_{exch}
4	X	X	X	X	cold	hot	t_{heat}
5	O	O	X	X	cold	hot	t_{exch}
Repeat Steps 2 to 5 for 4 times							
6	X	X	X	X	hot	cold	t_{heat}
7	X	X	O	X	hot	cold	$t_{\text{extr,Pd}}$
8	O	X	X	X	hot	cold	t_{exch}
9	X	X	X	X	cold	hot	t_{heat}
10	X	X	X	O	hot	cold	$t_{\text{extr,TiMn}}$

extraction rate was varied and the impact on the received integral product composition evaluated. As no impact was observed the extraction time is set to 10s and the sampling rate adapted accordingly. The composition of isotopes at the extraction port of each time step is integrated to determine the integral product composition. For the comparison of single separation experiments only samples of the column's end are compared. This is due to the utilized valve model implemented for the exchange valve, which does not allow for product extraction across the system border (c.f. Eq. (5.26)).

Grid Impact

To identify the required number of nodes, which allow for grid independent simulation results while consuming reasonable computational times, a representative HESTIA experiment was simulated and the number of nodes varied (normal operation mode, variant 4 in Fig. 4.8, Tab. C.1 and C.3). In total six grid cases were evaluated, varying from 5 to 30 nodes which resemble compartment sizes of 3.5 % to 21 % of the total columns length. While the calculated temperature and pressure profiles were unaffected by the grid size, the obtained product compositions differ for the investigated node numbers. This is not surprising, as a larger grid size summarizes reflects a larger sample volume contained in each compartment within the column, thus the sharpness of the gas composition profile is lowered, leading to a grid influence on the obtained integral product composition. The described impact on the calculated molar fractions of the homo-isotopologues H₂ and D₂ for varying node numbers are shown in Figure 5.9 on the left hand side, while a normalized presentation is given on the right.

The grid impact drastically decrease with increasing number of nodes, reaching a plateau for node numbers greater than 25. The highest deviations to 30 nodes occur for the H_2 fraction withdrawn from the Pd column, reducing from 58.2 (5 nodes) to 3.3 % (25 nodes). Since the computation time is highly non linear dependent on the number of nodes, a trade-off between accuracy-to-computational effort is necessary. Larger node numbers cause simulation times which are out of scope for this work. In addition, at a node number of 30 for advanced simulation times, in some cases violation of the convergence criteria occurred thus the simulations were terminated. A node number of 50 did not allow for initialization. Therefore, for all performed simulations the node number is set to 20 to enable rapid design iterations, which are currently the focus of the CMH-TSA process development. Using 20 nodes causes a maximum deviation of 8 % for the H_2 fraction of the Pd column sample, while the remaining product species differ less than 4.1 %.

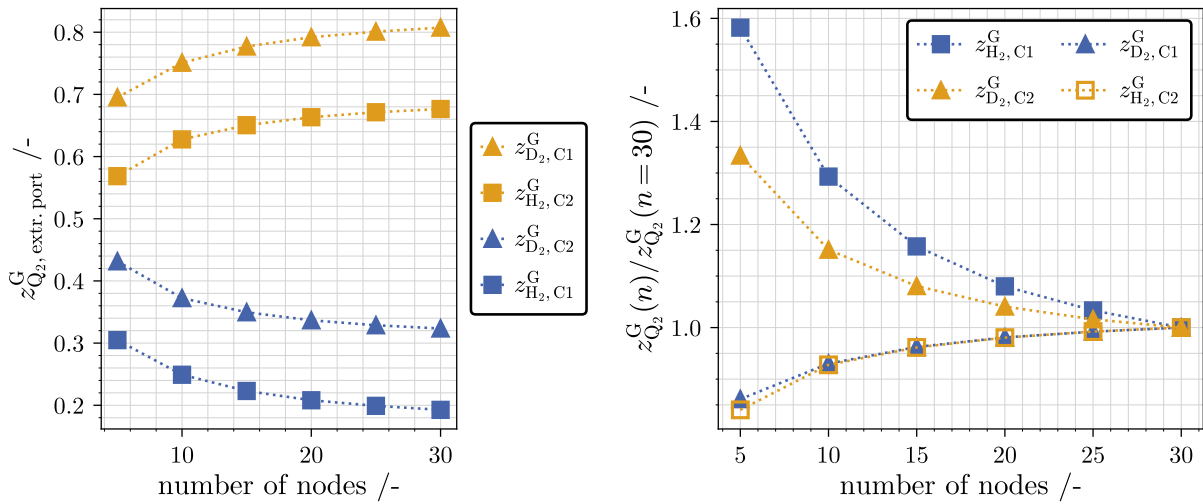


Figure 5.9: Left: Impact of node number on the obtained product compositions from Pd and TiMn column. Right: Deviations of obtained product composition for various grid sizes related to 30 nodes.

5.3.2 Simulation of Palladium Single Separation

The simulated and measured establishing T - and p -profiles within the Pd column and the PFR obtained for a separation experiment using only the Pd column (c.f. Subsec. 4.3.1 for detailed experiment evaluation, Fig. 4.6 Variant 1) are compared in Figure 5.10. The calculated pressure within the Pd column alternates between 42 mbar (absorption) and 1850 mbar (desorption), following the temperature changes, albeit not as instantaneous as observed during the experiment. For each cycle similar simulated plateau-pressure values are reached. The calculated pressure within the PFR alternates between the equilibration pressures obtained during the exchange steps, as the vessel is modelled without any material absorption capabilities. During depressurizing the Pd column an equilibration pressure of 500 mbar is reached, while 260 mbar establishes the other exchange way round.

No experimental PFR pressure profile is given in Figure 5.10 since no pressure sensor is installed at the PFR. However, the PFR pressure follows from p_2 connected at the Pd column during gas exchange. The deviation between simulated and experimental pressure at $t = 0$ min follows from the initialization state. While in an experiment all process Q_2 inventory is fed in the cooled Pd column resulting in the pressure at $t = 0$ min, the simulation time starts immediately after an equilibration, thus at the absorption pressure of the fully loaded Pd column (c.f. Subsec. 5.3.1). Therefore, the first experimental desorption pressure peak is significantly larger than the following peaks.

All simulated pressures of the different process steps are set into comparison to experimentally derived pressures in Table 5.4.

Implemented heating times of 10 min are sufficient to allow for establishing the targeted temperatures of absorption and desorption. The exchange phases are clearly marked by a down-peak in temperature during depressurizing and an up-peak for absorption within the simulated T -profiles. These follow from the heat of absorption during hydride formation and are not observable in the corresponding experimental T -profiles due to placement of the temperature sensor within the HESTIA columns (c.f. Subsec. 4.5), while clearly measurable during MAIA investigations.

The establishing absolute experimental temperatures and absorption pressures are in agreement with the simulated profiles, however, the experimental desorption pressures are underestimated by 28.2% from the simulation. This might be caused by the increasing deviations of the implemented equilibrium pressure correlation obtained for elevated temperatures (c.f. Subsec. 5.2.1).

Table 5.4: Simulated pressures at $x = L_{\text{col}}/2$ establishing during the different process steps of a Pd single separation experiment in comparison to experimental values.

Phase	$p_{\text{Pd,sim}} / \text{mbar}$	$p_{\text{exp}} / \text{mbar}$
Desorption	1850	2372 ± 52
Absorption	42	27 ± 1
Exch. Pd $\rightarrow$ PFR	500	475 ± 1
Exch. PFR $\rightarrow$ Pd	260	234 ± 0.2

Comparing the temporal evolution of the experimental T - and p -profiles to the simulated profiles, some deviations are observed. First, the experimental cycling times are not constant over the whole separation experiment, i.e., $t_{\text{cyc,exp}} = 26.8 \text{ min} \pm 2.5 \text{ min}$. Especially the time necessary for heating is shorter than that required for reaching absorption temperatures. In contrast, the simulated cycle time is always equal, i.e., $t_{\text{cyc,sim}} = 24 \text{ min}$. Second, since the experimental cycling time is larger, as a consequence, an increasing

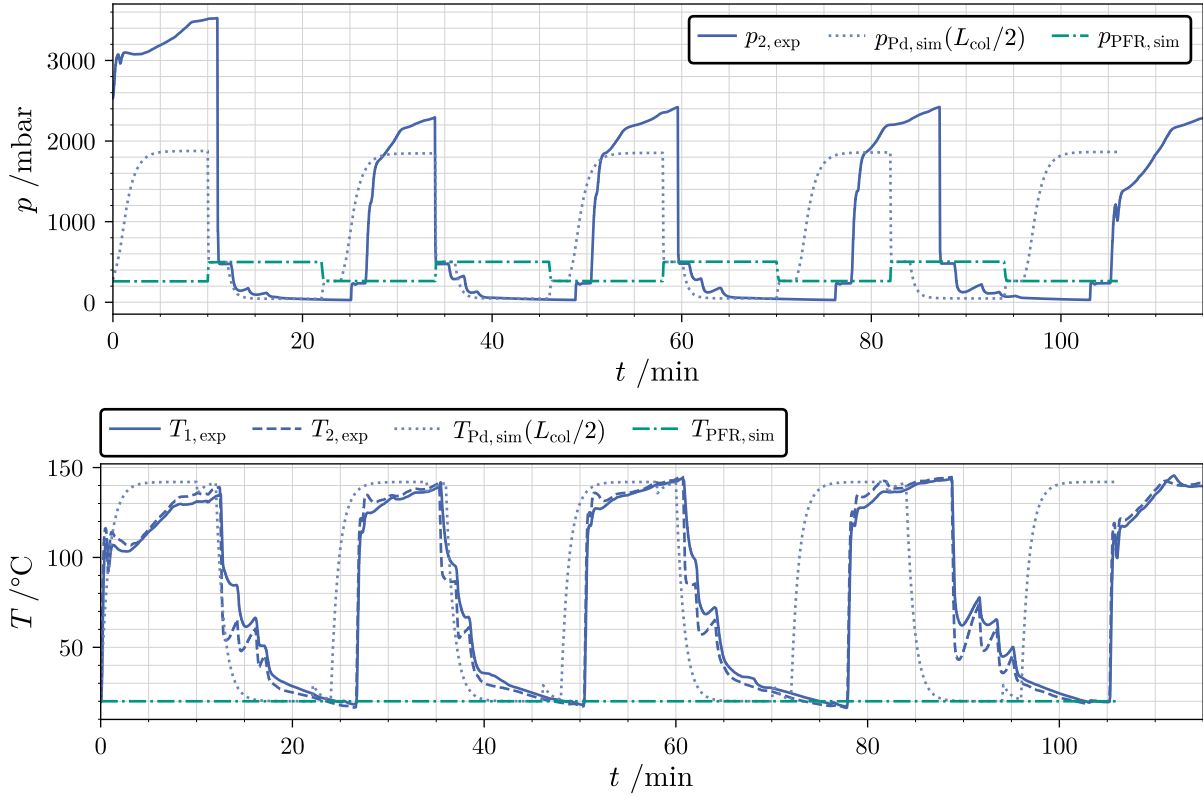


Figure 5.10: Comparison of simulated pressure (top) and temperature (bottom) profiles to temporal experimental data of a Pd single column separation experiment performed in HESTIA. Simulated profiles reflect establishing values in the columns mid, i.e., at $x = L_{\text{col}}/2$. Experimental parameter labels refer to HESTIA sensor tags given in Figure 4.2. Error bars are smaller than the line width.

shift over the whole separation experiment between measured and simulated profiles can be observed. Third, regarding the experimental T -profiles, whenever desorption phase is triggered, a temperature jump is noticeable. This jump is followed by a short down peak of 10 to 20 °C which merges into an almost linear heating rate until the set-point desorption temperature is reached. In contrast, the simulated ideal heating rates do not show any sudden jumps or peaks. This experimental phenomena can be explained by the utilized heating system of HESTIA. In total two oil baths are used to provide the required heat within processing. The heated oil is circulated through a double-walled heat exchanger surrounding the absorption column. When switching to desorption temperature, the cooled oil in the piping is immediately replaced by hot oil from the first bath having a temperature of ~ 180 °C, thus a large temperature delta to allow for rapid cycling. However, the oil bath is cooled by the recycled cool oil, as a combined heating system is used in HESTIA, thus the heating and cooling circuits are not separated (c.f. detailed P&ID in B.2 and Subsec. 4.1.2). Therefore, as soon as the oil bath temperature of the first bath falls below the temperature of the second bath, which is heated to the set-point temperature of 150 °C, the oil supply is switched to the second bath. This

manual operation and switch between the oil baths cause the observable decrease in the T -profile. The observed linear heating rate can be correlated to the heating rate of the utilized oil bath. In addition, as discussed in Section 4.3 and 4.4, the targeted desorption set-point temperature of 150°C is not achieved in the experiment. Therefore, the implemented desorption temperatures T_{hot} in the corresponding simulation case is adapted to the measured experimental temperatures accordingly to allow for unbiased pressure comparison. Finally, no smooth cooling rates are achieved during the experiment, instead several temperature jumps occur. This is again caused by the manual cooling operation. When switching to the absorption temperature, hot oil is directly routed into the chillers oil reservoir. An upper bath temperature of 40°C can be tolerated by the chiller, which is overreached if the hot oil ($T_{\text{oil}} = 150^\circ\text{C}$) is continuously processed from the heat exchanger to the chiller bath. Therefore, the column is cooled stepwise, such that the chiller has to handle only small batches of hot oil, to respect its upper temperature limit. As soon as the Pd column temperature falls below ~ 70 to 80°C the cooling power of the chiller is sufficient to allow for continuous circulation of the heat exchanger. Thus, most of the described temporal profile deviations are a consequence of the undersized coupled heating and cooling system of HESTIA which requires optimization (c.f. Sec. 4.5).

Nevertheless, the model outputs of highest interest are the estimated product composition extracted from the Pd column. During the experiment a molar protium fraction of 0.263 was measured. The simulated value differs only by 7.6 %, thus a molar fraction of 0.283 was calculated.

All in all it can be concluded, that the presented CMH-TSA model is capable to estimate with sufficient accuracy reachable product compositions and operation parameters for an absorption column which shows reproducible material behavior, i.e., the Pd column investigated in HESTIA.

5.3.3 Simulation of $\text{TiMn}_{1.5,\text{mod}}$ Single Separation

To simulate the single separation efficiency of the TiMn column in HESTIA (Fig. 4.6 Variant 2), three simulation cases were investigated, reflecting the different assumed $\text{TiMn}_{1.5,\text{mod}}$ states in the HESTIA set-up (c.f. Sec. 4.5) and compared to experimental results presented in Subsection 4.3.3. First, ideal $\text{TiMn}_{1.5,\text{mod}}$ characteristic (Fig. 3.9) were exploited for estimating the process time dependent pressure and temperature evolution. Then the run was repeated modifying the implemented PCI characteristics to those obtained from Figure 4.4 and finally by implementation of a $\text{TiMn}_{1.5,\text{mod}}$ accumulation in the column centre. The accumulation within the columns mid is physically possible, since the volume of $\text{TiMn}_{1.5,\text{mod}}$ is roughly around 5 mL. Further on, the position at $L_{\text{col}}/2$ appears reasonable, as the mobile powder is transported by the gas pulses during gas

exchange, which impact reduce towards the column centre and thus allows for final material settling there. It should be noted, that a complete discharge of absorbing $\text{TiMn}_{1.5,\text{mod}}$ from the TiMn column appears to be another valid explanation for the missing separation capability. However, this hypothesis can be rapidly disproved, since all possible exits are protected by filters of $2\text{ }\mu\text{m}$ mesh size coupled with stainless steel 316L powder bulks of $5\text{ }\mu\text{m}$ particle size, ensuring a confinement of $\text{TiMn}_{1.5,\text{mod}}$ within the column. Additionally, material discharge would be noticeable through pressure drops and pump failures due to damage to the vent seats and pumping systems, which did not occur.

The resulting simulated p - and T -profiles of those runs are given in Figure 5.11 and compared to the experimental data.

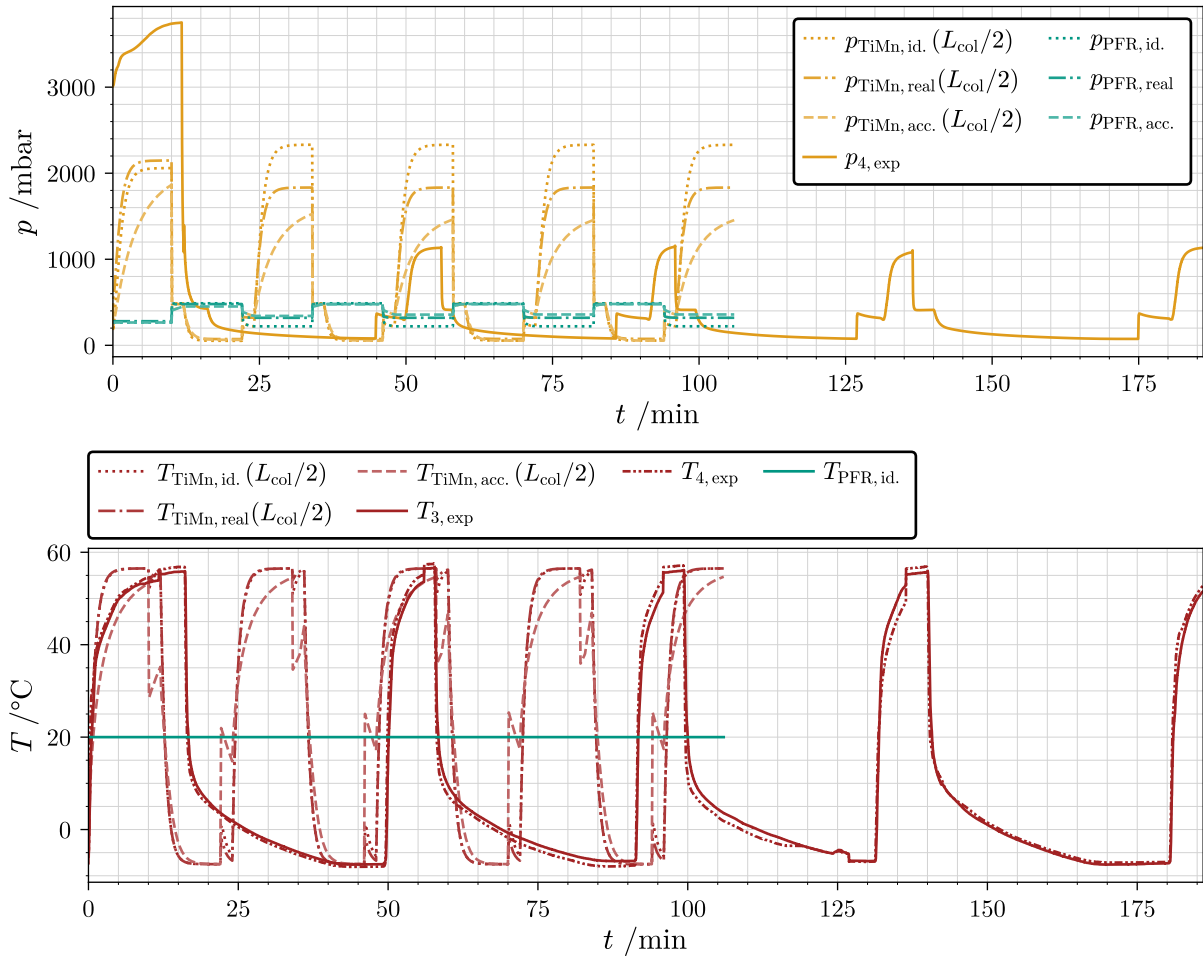


Figure 5.11: Comparison of simulated pressure (top) and temperature (bottom) profiles to temporal experimental data of a TiMn single column separation experiment performed in HESTIA. Three $\text{TiMn}_{1.5,\text{mod}}$ characteristics are investigated: ideal behavior (id.), contaminated surface (real) and accumulation (acc.) within the columns centre ($x = L_{\text{col}}/2$). Simulated profiles refer to establishing values in the columns mid, i.e., at $x = L_{\text{col}}/2$. Experimental parameter labels refer to HESTIA sensor tags given in Figure 4.2. Error bars are smaller than the line width.

While the simulated values of equilibration and absorption pressures are close to each other for the different cases and vary between 2 and 36.6 %, the desorption pressure estimation varies by 59.9 % the most. From course of $p_{\text{TiMn-acc.}}$ it can be seen, that the release of hydrogen from the accumulated $\text{TiMn}_{1.5,\text{mod}}$ is not completed within the given heating time. Although the obtained values show the lowest deviation to the experimental values (deviation of 28.4 %), this phenomenon is not expected during a HESTIA experiment, as the recorded pressure reached a plateau, indicating completed desorption. Furthermore, all calculated desorption pressures overestimate the experimental values. This might be caused by the deviation of set-point and effective gas temperature in the HESTIA column (c.f. Fig. 4.3). As concluded in Section 4.5, the installation of the temperature sensor is not ideal and additionally, non insulated parts of the column introduce temperature deviations. Therefore, the effective gas temperature is lower and causes lower pressures. Instead, the model assumes equal material and gas temperature (ideal system), which leads to higher simulated pressures. Table 5.5 set the simulated pressures for the different runs in contrast to the experimental values of the process steps.

Table 5.5: Simulated pressures at $x = L_{\text{col}}/2$ establishing during the different process steps of a $\text{TiMn}_{1.5,\text{mod}}$ single separation experiment in comparison to experimental values. Here, $p_{\text{TiMn-id.}}$ reflects ideal $\text{TiMn}_{1.5,\text{mod}}$ characteristics, while $p_{\text{TiMn-real}}$ represents contaminated $\text{TiMn}_{1.5,\text{mod}}$ and $p_{\text{TiMn-acc.}}$ assuming material accumulation in the column's mid.

Phase	$p_{\text{TiMn-id.}} / \text{mbar}$	$p_{\text{TiMn-real}} / \text{mbar}$	$p_{\text{TiMn-acc.}} / \text{mbar}$	$p_{\text{exp}} / \text{mbar}$
Desorption	2330	1833	1457	1135.7 ± 19.5
Absorption	55	75	55	76.2 ± 2.9
Exch. $\text{TiMn}_{1.5,\text{mod}}$ → PFR	490	480	480	412.5 ± 0.6
Exch. PFR → $\text{TiMn}_{1.5,\text{mod}}$	220	320	360	313.1 ± 1.8

The implemented set-point temperatures T_{hot} and T_{cold} are reached within the given heating and cooling times independent of the implemented $\text{TiMn}_{1.5,\text{mod}}$ characteristics. While the T -profiles of cases representing the ideal and real $\text{TiMn}_{1.5,\text{mod}}$ characteristics appear not to differ from each other, the T -profile of the accumulated $\text{TiMn}_{1.5,\text{mod}}$ case shows reduced heating rates. The exothermic hydride formation can be observed in the simulated data by temperature peaks during the exchange steps. Since the temperature at $x = L_{\text{col}}/2$ is depicted, the peak is more distinct for the simulation case of accumulated $\text{TiMn}_{1.5,\text{mod}}$. In this case, the whole $\text{TiMn}_{1.5,\text{mod}}$ amount is located at $x = L_{\text{col}}/2$ thus the heat evolvment does not distribute over the whole columns length. Similar to the Pd column single experiment, this peak is not observable within the experimental data due to temperature sensor placement.

Most of the observable deviations between the temporal evolvement of the experimental and simulated T - and p -profiles are caused by the heating and cooling system as detailed in the previous section for the Pd column experiment to simulation comparison. Therefore, only some observation unique for the TiMn column processing are highlighted in the following. The most obvious observation are the extended cooling rate which significantly increased the cycling time during the experiment. These are caused by operating at the minimum operational temperature of the utilized thermooil. Thus a reduced temperature delta between column and cooling media is exploited when approaching to the absorption set-point temperature. However, no jumps within the cooling rate occurs, as the oil can be circulated instantaneous through the heat exchanger and chiller bath. This is because the desorption temperature of the TiMn column equals around 60 °C such that the chillers upper temperature limit is not reached when switching the TiMn columns set-point temperature. Another TiMn column typical phenomenon are slower and therefore observable sorption kinetics. These are for example visible in the experimental p -profile at $t = 127$ to 132 min and $t = 175$ to 181 min. As concluded in Section 4.5 inhibited sorption kinetics may be caused by contaminations of $\text{TiMn}_{1.5,\text{mod}}$ filled in HESTIA. Therefore, longer exchange times of ~ 5 min were processed, while 2 min are implemented in the model. All in all, experimental cycling times of $t_{\text{cyc,exp}} = 43.8 \text{ min} \pm 4.1 \text{ min}$ result, thus almost a doubled time amount is required than assumed in the simulations ($t_{\text{cyc,sim}} = 24 \text{ min}$).

Comparing the resulting molar H_2 fractions (c.f. Tab. 5.6), it can be concluded that ideal $\text{TiMn}_{1.5,\text{mod}}$ would cause a concentration profile over the column as Pd does. In addition, the obtained reduction in the H_2 fraction for real $\text{TiMn}_{1.5,\text{mod}}$ behavior supports the assumption of separation efficiency inhibition by contaminated surfaces (c.f. Sec. 4.5) [46, 45]. However, even with the reduced isotope effect, a concentration profile should still be measurable according the simulation results. Finally, only the accumulated simulation leads to the observed absence of the profile, thus supporting the conclusion of contamination and accumulation due to mobile $\text{TiMn}_{1.5,\text{mod}}$ powder within the TiMn column in HESTIA (c.f. Sec. 4.5).

These conclusion are in agreement to the results obtained for 8 performed cycles as can be concluded from the results shown in Table 5.6. The separation efficiency should increase with more cycles. Poisoned material still exhibits a slight separation capability, while accumulation suppresses a contrary enrichment on the column's end, thus enabling only one separation stage.

From the described observation, it follows that a mixture of the assumed aspects (shifted sorption characteristics due to contamination and accumulation due to mobility) causes

Table 5.6: Comparison of simulated and experimentally obtained H_2 molar fractions in the product sample withdrawn from the TiMn column during a single column separation experiment. $z_{\text{TiMn-id.,H}_2}^{\text{G}}$ results from ideal $\text{TiMn}_{1.5,\text{mod}}$ characteristics, $z_{\text{TiMn-real,H}_2}^{\text{G}}$ reflects contaminated $\text{TiMn}_{1.5,\text{mod}}$ and $z_{\text{TiMn-acc.,H}_2}^{\text{G}}$ assumes accumulation in the column's mid. Given results represent a sample amount of 3.5 % (5 cycles) and 3 % (8 cycles) of the total inventory.

	$z_{\text{TiMn-id.,H}_2}^{\text{G}}$	$z_{\text{TiMn-real,H}_2}^{\text{G}}$	$z_{\text{TiMn-acc.,H}_2}^{\text{G}}$	$z_{\text{exp,H}_2}^{\text{G}}$
5 cycles	0.682	0.653	0.512	0.519
8 cycles	0.717	0.667	0.511	0.510

the lowered or even missing isotope effect of $\text{TiMn}_{1.5,\text{mod}}$. In the following section, only the results of simulations of ideal and accumulated $\text{TiMn}_{1.5,\text{mod}}$ are compared, since the latter has the largest impact on the separation efficiency, as identified in this section.

5.3.4 Simulation of Pd - $\text{TiMn}_{1.5,\text{mod}}$ Separation

Two HESTIA separation experiments (Variant 4 and 5, c.f. Fig. 4.8) are mimicked by simulation runs and compared in the following. First, the normal operation mode (c.f. Subsec. 4.4.2, Variant 4) and second, the modified gas exchange over the end of the desorption column (c.f. Subsec. 4.4.4, Variant 5) to evaluate the impact of gas phase composition on the separation. $\text{TiMn}_{1.5,\text{mod}}$ characteristics were assumed either ideal or reflecting accumulation, as this was determined to cause the suppression of multi-stage separation efficiency and considered as worst-case scenario. The obtained results for the process pressures and obtained product fractions of simulation and experiment are compared in Table 5.7 and 5.8 for both operation variants, respectively.

Due to the temporal deviations observed between experimental and simulation data detailed and discussed in the previous subsections for the single column studies, for sake of clarity, the temporal experimental profiles will not be shown in the following. A renewed discussion of the shift between the experimental and simulation cycle times is obsolete, as the same reasons, i.e., undersized and coupled heating and cooling circuits, are valid. Furthermore, since both columns are counter-cyclical heated, both limiting cooling rates (Pd and TiMn colum) impact the total process time. Thus, the temporal shift between experiment and simulation increases for progressing process time. Instead, the measured pressure and temperature values at the end of each process step for all performed cycles are depicted in Figure 5.12 and 5.13 at the corresponding normalized cycle time as single measurement point respectively. This allows for an comparison of the establishing absolute operational parameters mimicked by the simulation cases for the simulated operation scenarios investigated.

Normal Operation

In both normal operation mode simulation cases, pressures within the Pd column reach plateaus during absorption and desorption. While for absorption the simulations only differ by 11.3 % from each other, the obtained desorption pressures values deviate from 2915 mbar (ideal $\text{TiMn}_{1.5,\text{mod}}$ behavior) to 2669 mbar (accumulated $\text{TiMn}_{1.5,\text{mod}}$). The heating and cooling times are chosen sufficiently large to reach the set-point temperatures for Pd. The heat of formation during hydride formation and desorption is observable by temperature peaks occurring at each exchange step. The experimental pressures obtained within the Pd are less accurately represented by the ideal $\text{TiMn}_{1.5,\text{mod}}$ simulation case and differ about 4.9 %, while the accumulated $\text{TiMn}_{1.5,\text{mod}}$ scenario pressures differ by 3.8 %.

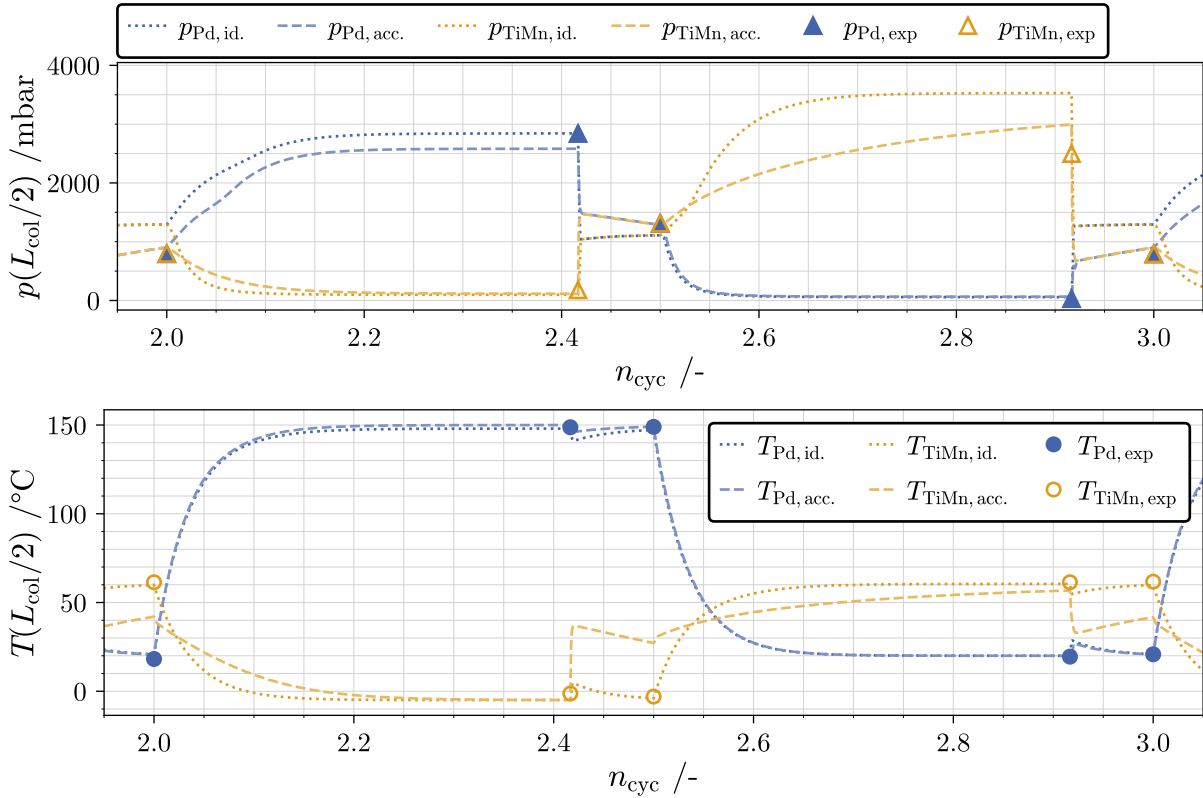


Figure 5.12: Simulated pressure (top) and temperature (bottom) profiles at $x = L_{\text{col}}/2$ of the normal operation HESTIA experiment compared to experimental values for a representative cycle (full size in Fig. C.1). $\text{TiMn}_{1.5,\text{mod}}$ characteristics are respected by ideal behavior (id.) in comparison to accumulation (acc.) within the columns centre ($x = L_{\text{col}}/2$). Error bars are smaller than the markers.

The resulting simulated p and T profiles for the TiMn column differ from each other for the investigated runs. For the ideal $\text{TiMn}_{1.5,\text{mod}}$ behavior, absorption and desorption pressures reach plateaus within the heating times. However, for both $\text{TiMn}_{1.5,\text{mod}}$ states the simulated desorption pressures overestimate the experimentally obtained values by 43.3 % (ideal) and 22.3 % (accumulated) (c.f. Tab. 5.7). Due to the accumulation, the desorption

rates are inhibited, which is also observed for the $\text{TiMn}_{1.5,\text{mod}}$ single separation evaluation and observable by the pressure slope during the exchange phase in the simulated profiles. These do not occur for ideal characteristics, instead instantaneous pressure equilibration is visible. While the depressurizing of the Pd column is more accurately represented by both simulated cases (deviation is 18.5 % maximum), the equilibration during pressurized TiMn column is overestimated up to 57.7 % (ideal) by both. However, in general, the simulation case of accumulated $\text{TiMn}_{1.5,\text{mod}}$ reflects experimental values more accurately.

The differing pressure values of simulations and experiment, especially for desorption and equilibration pressures, are correlated to the deviation between experimental temperatures and ideal temperature conditions during simulation, as discussed in Subsection 5.3.2 and 5.3.3. This phenomenon is less distinct for combined column separation experiments, as the higher equilibrium pressures of contaminated $\text{TiMn}_{1.5,\text{mod}}$ might reduce the resulting pressure difference following from ideal and real experimental temperature. Thus, two competing effects (contaminated $\text{TiMn}_{1.5,\text{mod}}$ and temperature deviation) have an impact on the desorption pressures, complicating an isolated interpretation of the resulting values.

Nevertheless, the resulting enrichments of the extracted product fractions of each column allow for supporting the assumption of accumulated $\text{TiMn}_{1.5,\text{mod}}$. For ideal $\text{TiMn}_{1.5,\text{mod}}$ behavior, the inverse isotope effect is present, as a higher H_2 proportion is obtained in the $\text{TiMn}_{1.5,\text{mod}}$ product composition. While for ideal $\text{TiMn}_{1.5,\text{mod}}$ properties the enrichment differs by 16.3 % in the second case (accumulated $\text{TiMn}_{1.5,\text{mod}}$) only 2.1 % deviation is observed. The H_2 composition in the product extracted from the Pd column is also more accurately reflected by the accumulation case (deviation of 24.9 %). The concluding evaluation on the impact on the obtainable enrichment by the introduction of the second active TiMn separation column for the HESTIA set-up is given in Subsection 5.3.5.

Exchange Variation

The calculated process parameter profiles for this operation mode (Variant 5) are set in relation to experimental data in Figure 5.13. Again, the implementation variant of the $\text{TiMn}_{1.5,\text{mod}}$ characteristics lead to differing pressure profiles. It reveals that the experimentally obtained Pd pressures are better reflected by the ideal $\text{TiMn}_{1.5,\text{mod}}$ case. In contrast, the $\text{TiMn}_{1.5,\text{mod}}$ desorption pressures are more accurately depicted by the accumulated material simulation. These differ by 18.2 % instead of 67.9 %.

Again, for mobile $\text{TiMn}_{1.5,\text{mod}}$, the pressures in the TiMn column do not reach a pressure plateau for the given heating times, thus the sorption rates of $\text{TiMn}_{1.5,\text{mod}}$ inhibit the gas exchange.

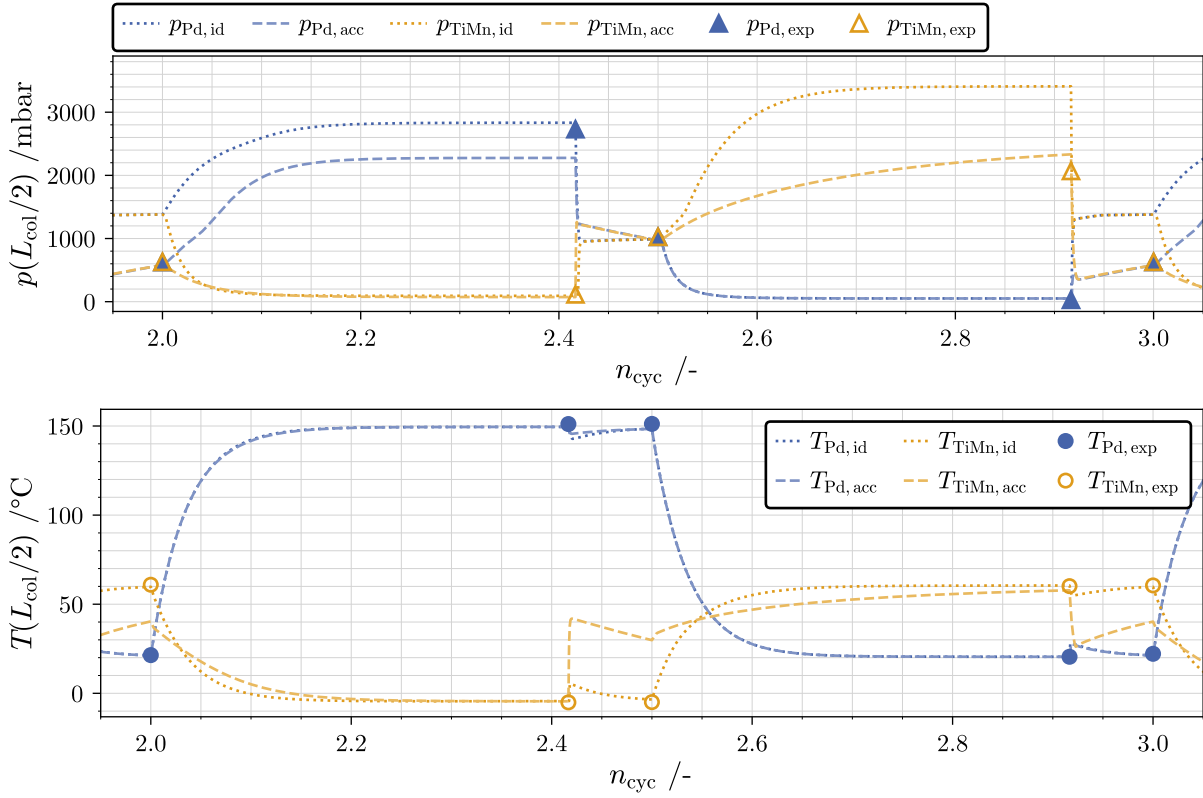


Figure 5.13: Simulated pressure (top) and temperature (bottom) profiles at $x = L_{col}/2$ of the exchange variant HESTIA experiment compared to experimental values for a representative cycle (full size in Fig. C.2). $TiMn_{1.5,mod}$ characteristics are respected by ideal behavior (id.) in comparison to accumulation (acc.) within the columns centre ($x = L_{col}/2$). Error bars are smaller than the markers.

Both simulation cases deliver lowered separation efficiency in comparison to the normal operation mode and the same conclusion as obtained from the experiment as described in Subsection 4.4.4, thus the modification of the gas transfer route between the columns does not support the separation effect and counteracts the enrichment. The enrichment in D_2 in the Pd column is overestimated by both simulations as in the normal operation simulation, while the composition of the $TiMn_{1.5,mod}$ product is more accurately displayed by the accumulated $TiMn_{1.5,mod}$ simulation (2 % deviation to 11.7 %).

Although the qualitative impact on separation efficiency is in agreement for simulations and experiments and the assumption of accumulated $TiMn_{1.5,mod}$ further strengthened, the results differ more than in normal operation mode. This might be caused by the not respected piping of HESTIA. Due to the utilized bypass for realizing an exchange variation, an increased re-mixing and non processed residual gas portion remains in the piping. During normal operation about 2 to 3 % of the total processed hydrogen inventory remains in the exchange piping, while it increases to 9 to 15 % for the modified exchange route, causing reduction in the measured separation efficiency. In the simulation set-up,

the exchange route volumes are equal. Therefore, the enrichment is overestimated. Nevertheless, the simulation results show that this operation mode is even for ideal settings less separative than the normal mode, thus supporting the conclusion from the experimental evaluation. From these conclusion follows, a CMH-TSA process operation according Variant 3 is more efficient concerning the reachable product enrichment.

Table 5.7: Overview of simulated pressures at $x = L_{\text{col}}/2$ establishing for different process steps during a separation experiments using both columns in comparison to experimental values. $p_{\text{TiMn-id.}}$ refers to simulation case of implemented ideal $\text{TiMn}_{1.5,\text{mod}}$ characteristics and $p_{\text{TiMn-acc.}}$ to material accumulation in the column middle ($x = L_{\text{col}}/2$).

Phase	Column	$p_{\text{TiMn-id.}} / \text{mbar}$	$p_{\text{TiMn-acc.}} / \text{mbar}$	$p_{\text{exp}} / \text{mbar}$
Normal Exchange (Variant 4)				
Desorption	Pd	2915	2669	2777 ± 83
	TiMn	3542	3022	2471 ± 24
Absorption	Pd	53	59	31 ± 2
	TiMn	97	109	164 ± 21
Exchange	TiMn $\rightarrow$ Pd	1252	850	795 ± 13
Exchange	Pd $\rightarrow$ TiMn	1100	1250	1351 ± 70
Exchange over column's ends (Variant 5)				
Desorption	Pd	2931	2298	2737 ± 27
	TiMn	3471	2443	2067 ± 39
Absorption	Pd	49	50	30 ± 1
	TiMn	92	73	128 ± 12
Exchange	TiMn $\rightarrow$ Pd	1370	550	632 ± 6
Exchange	Pd $\rightarrow$ TiMn	980	980	1028 ± 37

5.3.5 Conclusion of HESTIA Simulations

The presented CMH-TSA model was validated stepwise starting on sub-model level and progressing to HESTIA imitation. $\text{H}_2\text{-D}_2$ separation experiments performed in HESTIA, including single column and combined column separation experiments exploiting different operation scenarios, were successfully simulated, demonstrating the models flexibility and stability.

While the stand-alone Pd column simulation confirmed the model accuracy concerning the molar product composition (deviation by 7.6 %), the corresponding stand-alone TiMn column simulations allowed for further interpretation of the $\text{TiMn}_{1.5,\text{mod}}$ state within the HESTIA set-up. By comparing the resulting product compositions of the three different

Table 5.8: Overview of resulting H_2 molar fractions within the product simulation for simulation cases representing a separation experiment of both columns and compositions measured during HESTIA experiments.

	Normal exchange (Variant 4)		Exchange columns end (Variant 5)	
	$z_{\text{H}_2, \text{Pd}}^{\text{G}}$	$z_{\text{H}_2, \text{TiMn}}^{\text{G}}$	$z_{\text{H}_2, \text{Pd}}^{\text{G}}$	$z_{\text{H}_2, \text{TiMn}}^{\text{G}}$
TiMn _{1.5,mod} -id.	0.214	0.663	0.314	0.477
TiMn _{1.5,mod} -acc.	0.251	0.558	0.325	0.430
Experiment	0.334	0.570	0.455	0.487

simulation cases, the assumptions that TiMn_{1.5,mod} in HESTIA is contaminated and accumulated (c.f. Sec. 4.5) were strengthened. This non ideal state leads to a reduction in separation efficiency from a multi-stage separation column to a single separation stage. Meanwhile, the theoretical multi-stage separation efficiency for ideal TiMn_{1.5,mod} behavior showing an inverse isotope effect was verified.

By utilizing this identified TiMn_{1.5,mod} state, it succeeded to simulate the observed experimental product compositions withdrawn during HESTIA experiments using both columns (c.f. Tab. 5.8). However, the largest deviations up to $\sim 60\%$ between simulated and measured values occurred for the operational pressures. These were attributed to the non-ideal gas temperature distribution observed in the HESTIA columns (c.f. Fig. 4.3), which were not taken into account in the model, as well as deviations between the implemented equilibrium pressure model and measured PCIs (c.f. Subsec. 5.2.1). Therefore, to optimize the presented CMH-TSA model in future, further material characterization measurements to increase the data for determining the model parameters as well as an optimized CMH-TSA set-up (c.f. Sec. 4.5) is suggested.

The results of the different gas exchange variations investigated in HESTIA and the corresponding simulations lead to the conclusion that the gas chromatographic effect (supported by isotope exchange reactions) is the determining driving force of separation, which is also stated in [56]. This is revealing when comparing normal operation (Variant 4, Fig. 4.8) to a gas exchange route across the column's end (Variant 5), causing internal isotope exchange and displacement chromatography, which reduces the product enrichments as presented in Table 5.8. Therefore, Variant 4 is the most promising operation mode and used in Section 5.4 to demonstrate the impact of the second active separation column on the reachable product composition in contrast to a stand-alone Pd column operation.

5.4 Impact of Second Separation Column with Inverse Isotope Effect

The validated CMH-TSA model allows for evaluating the impact on the separation efficiency by coupling the Pd column with a second active separating column filled with $\text{TiMn}_{1.5,\text{mod}}$ material, which has an inverse isotope effect during its hydride formation. To do so, the HESTIA column geometry and the normal operation mode (Variant 4, c.f. Fig. 4.8) are utilized. The latter proved to be the most promising operation mode, which is therefore also envisioned for large scale application. The simulation routine presented in Table 5.3 was used to simulate the obtainable product composition for a stand-alone Pd column (head and bottom product) in comparison to the product compositions withdrawn from both separation columns, i.e., a Pd column coupled with a TiMn column, separating an equimolar H_2 - D_2 -mixture. The analyzed operated Q_2 inventory and sampled product amount were oriented on the processed amounts during a HESTIA experiment and are given with all utilized initialization and model parameters in Table C.3 in the appendix.

In Table 5.9 the obtained simulated product compositions for each scenario are compared. Both product enrichments obtained from a single operated Pd column are significantly increased by exchanging the gas phase with the TiMn column for similar process operation conditions. This means, the product withdrawn from the Pd column (which equals the product sample from the Pd column bottom during single operation) is further depleted in its H_2 content by 35.9 %. In contrast, the product sampled from the TiMn column (which equals the product obtained from the Pd column top during single operation) shows an increase in its H_2 enrichment by 23.9 %. Thus it can be concluded that the CMH-TSA process which is extended by a second active separation column shows optimized product enrichment, which was stated in hypothesis 2.

Table 5.9: Comparison of simulated molar product compositions withdrawn from a stand-alone Pd separation column from column top and bottom (c.f. Fig. 2.4, a)) to product compositions obtained from a Pd and TiMn column in an CMH-TSA set-up (c.f. Fig. 2.4, b)).

Product composition	Stand-alone Pd Column	Coupled Pd and TiMn columns
$z_{\text{H}_2}^{\text{G}}$ rich product	Pd top: 0.531	TiMn: 0.658
$z_{\text{H}_2}^{\text{G}}$ depleted product	Pd bottom: 0.276	Pd: 0.203

Beside the obtained impact on the reachable product compositions, the simulated profiles of the Q_2 loading in the absorption materials should be highlighted. Regarding those c profiles of both columns shown in Figure 5.14, it is noticeable that both materials are not significantly de-loaded during their isolated change to desorption (closed exchange valve).

This means, the available free gas volume for expansion is not sufficient to capture the complete hydrogen amount absorbed in the material lattices in the previous process step. Only when opening the exchange valve and bringing the gas phases of both columns in contact to each other, the material in desorption phase is sufficiently emptied by the second partner material in absorption phase. This can be seen by the instantaneous increase of concentration in the cooled material and the corresponding decrease of the material in desorption phase, thus a hydrogen transfer from *lattice-to-lattice*.

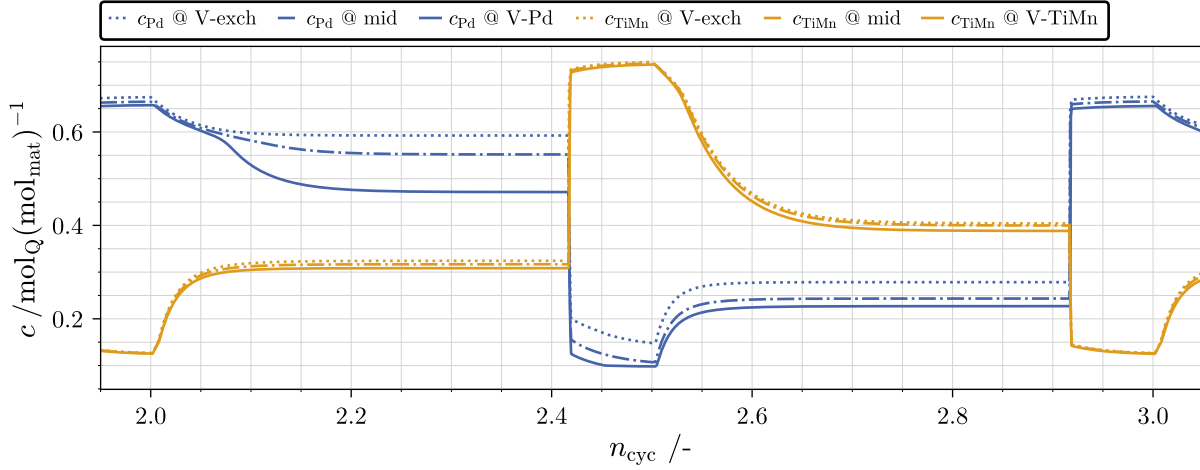


Figure 5.14: Establishing concentration profiles of absorbed hydrogen in the metal lattice at different locations within each absorption column during a normal operation HESTIA experiment for a representative cycle.

From this observation it is concluded, that the isolated process step to realize phase changes accompanied by a temperature switch, i.e., Steps III and V (c.f. Tab. 2.1), can also be executed at permanently open exchange valve. Thus, a continuous interaction and gas transfer between the columns is allowed, which simplifies the process routine, reduces the number of movable components, i.e., valves, and increases the system throughput. This optimized operation mode is only enabled when using a second active separation column, as discussed in more detail and evaluated in Chapter 6 for a large scale CMH-TSA set-up, representing a relevant IRPR system size.

Chapter 6

Scale-Up of CMH-TSA Process for EU-DEMO IRPR

In the previous chapter, a robust and versatile CMH-TSA process model was developed and validated using experimental data of MAIA and HESTIA campaigns. This model, extrapolated by tritium relevant characteristics, is now used to evaluate the CMH-TSA technology to serve for large scale operation on the example of the IRPR system for EU-DEMO (hypothesis 4). In addition, a preliminary design of CMH-TSA unit for this system shall be proposed. As learned from the HESTIA simulations, the key benefit of the second active separation column is the enhanced capability of pumping the partner column, while contributing to the chromatographic separation efficiency. This optimization potential was in addition addressed in Subsection 2.2.3, while the dominating chromatographic effect caused by a flow through the separation column was concluded from single Pd column experiments described in Subsection 4.3.2. Therefore, an advanced process operation mode is introduced, which serves as solution for the TCAP throughput limitations. After describing the investigated operation mode, the column design is presented and the selected model parameters discussed. Then, the simulated operation profiles, resulting compositions and extractable amounts are evaluated. These results allow for sizing and scale-up of the CMH-TSA process for the IRPR system.

6.1 Operation at Continuous Gas Exchange

By extending the TSA process of a second active hydride forming material, an operation method is possible, which allows for continuous interaction between the columns. In this mode, the exchange valve V – Exch (c.f. Fig. 2.4) is replaced by an orifice or permanently open during processing, instead of alternating its position as described in Table 2.1. The occurring gas transfer between the column is determined by the respective temperatures

and continuously adapting. If the process temperatures and material amounts in the columns are optimally adapted to each other, the materials have the ability to pump each other. This leads to very low residual, non-processed isotopes in the material lattice during desorption phase, which reduces non-operated tritium inventory. Thus, instead of separately releasing hydrogen into the free gas volume of the column during desorption or absorbing remaining gas from the previous exchange step, the isotopes are rather transferred from *lattice-to-lattice*. This reduced the necessary void space for containing the desorbing gas. In other words: The columns can be completely filled with active absorption material until an ideal packing of spheres is reached. This in turn significantly increases the processable amount of hydrogen.

In contrast to that, this operation variant is not realizable in a TCAP. Since the inert PFR does not exhibit the capability to pump, all process parameters are adapted by the Pd column. To enable a sufficient gas transfer between the columns, absorption and desorption temperatures have to be selected accordingly. In addition, residual hydrogen inventories in the Pd columns cannot be avoided [54]. Further advantages are expected from this modification, which are described in detail in the following.

Reduced Pressure Peaks

The pressure peaks resulting during desorption phase are significantly reduced, since the released gas immediately travels to the partner column in absorption phase. The maximum pressure is limited by absorption pressure for the revealing concentration in this material.

Reduced Temperature Amplitudes

Also, lower temperatures for desorption and higher temperatures for absorption are sufficient, as the materials pump each other. In contrast, the TCAP requires the temperature introduced driving force for the gas exchange, to enable sufficient pressure difference between the active Pd column and the inert PFR.

Reduced Energy Consumption

As the delta of both temperature amplitudes is reduced, the energy consumption of the process is significantly lowered.

Reduced Number of failure-prone Components

Less components for process control are necessary, while monitoring is simplified. Failure and maintenance of movable components are avoided and the system complexity is reduced.

Increased System Throughput

Beside the higher amounts of absorption materials within the columns, which allow for

increased system throughput as larger hydrogen inventories are processed within one column pair, the process times required for the temperature changes are shorter. This is due to the lowered temperature delta, which reduces the heating and cooling times, which have the main contribution to the necessary cycling time [103]. Thus, the total process time is lowered, which in turn increases the time-averaged system throughput.

The resulting process step scheme as used for the CMH-TSA simulation investigated in this chapter is shown in Table 6.1. These automation steps follow in general the process operation described in Section 2.2. The reduction in control complexity can be seen by comparison to the utilized automation of a HESTIA simulation (c.f. Tab. 5.3).

Two figure of merits are important to evaluate the separation efficiency and fulfilment of the demanded separation task: The system throughput and the purity of each product composition, thus in combination the yield of the value species. For the separation task of the IRPR system the optimum of processable throughput and establishing product enrichment is searched.

Table 6.1: Process steps and valve position for a CMH-TSA operation mode under continuous gas transfer.

Step	V – exch	V – Pd	V – TiMn	V – Feed	T _{Pd}	T _{TiMn}	Time
1	O	X	X	O	cold	hot	t_{feed}
2	O	X	X	X	hot	cold	$t_{\text{heat}} + t_{\text{exch}}$
3	O	X	X	X	cold	hot	$t_{\text{heat}} + t_{\text{exch}}$
4	O	X	X	X	hot	cold	t_{heat}
5	O	O	X	X	hot	cold	$t_{\text{extr,Pd}}$
6	O	X	X	X	cold	hot	$t_{\text{exch}} + t_{\text{heat}}$
7	O	X	O	X	cold	hot	$t_{\text{extr,TiMn}}$

6.2 Configuration of CMH-TSA Base Unit

To propose a design of relevant scale for the CMH-TSA system unit, the following path is executed. First, a reasonable column geometry is chosen, which is not limiting the heat transfer and allows for maximized product enrichments. Then, the amount of active separation material is estimated by assuming an ideal packing of spheres, using the bulk density known for the investigated material couple. From this amount, the total absorption capacity, i.e., the total hydrogen inventory, is defined. As identified from preliminary simulations, the tolerable extraction amount equals 10 to 15 % of the total inventory, still allowing for re-establishing the composition within few additional closed loops. This

product amount is then time-averaged over the total process time, yielding the system throughput per column pair unit. From this stream, the total required number of parallel column systems follows from the IRPR stream to be processed ($= 11 \text{ Pam}^3/\text{s}$, c.f. Sec. 1.2). Thus, the scale-up is realized by parallelization of the base unit.

Degrees of freedom are the number of parallel columns, the amount of extraction and the number of closed loops after product extraction. So first, from the residence time of the INTL, the total acceptable combination of open and closed cycles numbers are derived. In general, additional closed cycles reduce the time-averaged system throughput and thus increase the number of parallel systems. However, in turn, extraction of less product amount also reduces the overall throughput. Therefore, a trade-off has to be identified for these conflicting figures of merit. The main design drivers and their impact on the process are summarized in Table 6.2 [54] and are respected for the preliminary design discussed in this section.

Table 6.2: Main column geometry design drivers and the corresponding impact on the CMH-TSA process [54].

Design driver	Impact
Column length	Product purification
Column diameter	Heating time and material amount
Material amount	Throughput
Number of closed cycles	Purification and throughput
Magnitude of temperature swing	Energy consumption and cycle time, i.e., throughput

6.2.1 Column Geometry

The design parameter responsible for the reachable purification is the length of the separation column. Therefore, to a reasonable size of 10 m in total is selected. TCAP column sizes described in literature vary by 4 m [70], 6.35 m [35] to 20 m [115]. In the predecessor work, column lengths of 3 and 6 m were utilized [26]. The diameter should be chosen as large as possible to increase the amount of material, without causing heat transfer limitations accompanied by longer heating times. Literature values are 0.95 cm [35] to 0.7 cm [70], while HESTIA is operated with 0.6 cm. A reasonable compromise is 1 cm, as the continuous gas exchange operation suppresses establishing insulating vacuum conditions (as occurring during isolated absorption phase). In addition, the permanent convective heat transport might support the heat conductivity of the hydride bed.

The absorption materials Pd and $\text{TiMn}_{1.5,\text{mod}}$ are assumed to be composites, allowing for ideal spheres with a diameter of $d_p=1\text{ mm}$, which is a standard size in heterogeneous catalysis reactors. This allows for compact ideal beds, increases the contained amount of absorption material and the contact surface for the gas-solid-exchange. To avoid wall effects during flow-through, a ratio of $10 < \frac{D_{\text{col}}}{d_p} < 15$ has to be selected. To determine the material amounts within the ideal packed columns, the bulk density of the Pd composite sample introduced in Chapter 3 is used for benchmark. Thus with a bulk density of $\sim 1.2\text{ g/mL}$, 30 weight percentage of active component, the above selected dimensions of the column and the molar mass of Pd $\tilde{M}_{\text{Pd}} = 106.4\text{ g/mol}$, a material amount of 0.27 mol/m column results. Taking into consideration that the to the column geometry adapted larger particle diameter in the IRPR system leads to a larger particle surface, an increased amount of Pd in the coating should be respected. The surface ratio between IRPR particles and HESTIA particles equals $A(d_{\text{p,IRPR}})/A(d_{\text{p,Pd,HESTIA}}) = 1.56$. Multiplying this factor with the afore calculated 0.27 mol/m , a material amount of 0.42 mol/m results. Therefore, a conservative amount of $N_{\text{mat,Pd}} = 4\text{ mol}$ is assumed. Pd and $\text{TiMn}_{1.5,\text{mod}}$ have comparable capacities, which can be concluded by comparing the PCIs of both materials in Figure 3.4 and 3.9, thus an equal amount of $\text{TiMn}_{1.5,\text{mod}}$ is required in the other column. Using the obtained reversible capacities for each column (C1 and C2) of preliminary simulation studies, i.e., the values of maximum saturation $c_{\text{max,abs}}$ and minimum concentration $c_{\text{res,des}}$ remaining in the column at terminated desorption phase, the total processed hydrogen inventory $N_{\text{Q}_2,\text{tot}}$ within the CMH-TSA base unit follows from

$$\begin{aligned} N_{\text{Q}_2,\text{tot}} &= 0.5 \cdot (c_{\text{max,abs}} N_{\text{mat,C1}} + c_{\text{res,des}} N_{\text{mat,C2}}) \\ &= 0.5 \cdot 4\text{ mol} (0.65 + 0.25) = 1.8\text{ mol} . \end{aligned} \tag{6.1}$$

The final processable Q_2 throughput from the described CMH-TSA unit geometry parameters follows from the product extraction amount, which is chosen to equal several per cent of the total inventory. The repeated withdrawn product fraction has to enable a re-establishing of the gas composition or in other words allows for a stable operation point without drifts in product composition over time. Therefore, extraction amounts up to 15 % are considered.

6.2.2 Operational Parameters

Process Temperatures

The temperature amplitudes are limited in several ways. First, a lower bound is given to exclude cryogenic temperatures. Instead, it is envisioned to enable standardized cooling

water application serving as driving force between the absorption temperature set-point and the cooling medium. Concerning the selection of desorption temperatures, which define the desorption pressures, the pressure difference required for the gas transfer between the columns has to be enabled and in addition enough pressure provided for the product extraction. Each product stream pressure has to allow for system integration to the connected downstream units as no additional pumping system is foreseen. For the product stream provided by the Pd column, i.e., the T₂ and D₂ enriched stream, a pressure of at least 900 mbar should be realized, as this is the mean pressure of the gas buffer vessel in the gas distribution unit. The other product stream of the TiMn column has to be extracted at slightly higher pressures of 1000 mbar, as the gas buffer vessel sampling the feed gas for the isotope separation system (cryo distillation columns) operates at this pressure level. The respective pressures are adapted by the desorption temperatures.

Having these design criteria in mind, preliminary investigations were performed. The results are optimal operation temperatures of 0 °C during absorption for both materials, while optimal desorption temperatures of 60 °C for TiMn_{1.5,mod} and 120 °C for Pd revealed, which refer to pressures of ~2000 mbar. During product extraction this pressure will slightly decrease, therefore the higher safety margin was chosen. The absorption pressures in turn revealed to be 69 mbar for Pd and 99 mbar for TiMn_{1.5,mod} (c.f. Fig. 6.4, total reflux $n_{cyc} < 10$).

The input composition investigated reflects those of the current design point of the EU-DEMO fuel cycle, thus molar fractions of $z_{feed,T_2}^G = z_{feed,D_2}^G = 0.495$ and $z_{feed,H_2}^G = 0.01$ are assumed [18].

Tolerable Number of Closed Cycles

From the mean residential time of the inner loop t_{INTL} , which is ~1.7 h, a total available process time of 6120 s follows [18]. The following times for the process steps are assumed conservatively and based on comparable TCAP data [35, 57] as well as experience governed from the HESTIA experiments and their supportive simulations.

- $t_{heat} = 400$ s, as the temperature swings are lower for a two column system and no cryogenic temperatures are needed. Also, due to the opened exchange valve, there is no insulating vacuum present.
- $t_{exch} = 200$ s, after reaching set-point temperatures, additional time is given for completing ongoing equilibration between the columns, as the chosen design is elongated.
- $t_{feed} = t_{extr,Pd} + t_{extr,TiMn} = 180$ s, since only 10 to 15 % of the total inventory are

withdrawn. This is a conservative estimation to provide enough time for feeding and product sampling. As those process times only equal 14 % of the total cycling time, the introduced deviation to the final real extraction and feed time is considered negligible on the resulting time-averaged system throughput.

For a closed cycle (Step 2 and 3 in Tab. 6.1), a total time of $t_{CC} = 1200$ s reveals, while a complete cycle (Steps 1 to 7) needs a process time t_{OC} of 2560 s. The tolerable number of additional repeated closed cycles following an open cycle $n_{CC,max}$ can be estimated from

$$n_{CC,max} = \frac{t_{INTL} - t_{OC}}{t_{CC}} \leq 2.97 . \quad (6.2)$$

Thus, the CMH-TSA process for the IRPR system only allows for 2 additional closed loops after performing an open cycle. Otherwise the CMH-TSA process time exceeds the residence time of the inner fuel cycle loop.

Split Ratio of Product Streams

Most of the processed hydrogen stream has to be rerouted to the gas distribution system. Therefore, a higher product amount is extracted from the Pd column. Also, to maximize the enrichment in H_2 in the $TiMn_{1.5,mod}$ product fraction, a smaller stream is withdrawn here. The ratio of the $TiMn_{1.5,mod}$ product stream to feed stream is introduced as split factor Ψ_{split}

$$\Psi_{split} = \frac{\dot{N}_{extr,TiMn}}{\dot{N}_{feed}} = 1 - \frac{\dot{N}_{extr,Pd}}{\dot{N}_{feed}} . \quad (6.3)$$

From the preliminary design point, assuming a separation efficiency of the IRPR system which allows for routing 90 % of the fed-in H_2 to the ISS, follows a suitable split ratio Ψ_{split} of 0.15, thus 85 % of the unit's throughput is withdrawn from the Pd column [22].

6.3 Discussion of Simulated Process Parameter and Enrichment Profiles

In the previous section, the baseline CMH-TSA unit was presented. Using this geometry and temperature selection, the impact of extracted product fraction and the number of closed cycles on separation efficiency is explored by simulations using the CMH-TSA model presented in Chapter 5. All discussed operation schedules, i.e., variations of product sample amounts and performed closed cycles, are exploiting the optimized operation mode enabling a continuous gas exchange as introduced in Section 6.1. The utilized initialization parameters are given in Table C.4 in the appendix. First, the CMH-TSA unit is allowed to run into steady state, which requires ~ 10 cycles in total reflux mode. First,

the characteristics of this closed loop steady state are presented. Then the establishing operational points concerning process pressures, temperatures and product enrichments are discussed for the various sampling amounts and closed cycles. From these findings, the resulting required IRPR system size is concluded in Section 6.4.

6.3.1 Process Parameter Profiles

Steady State of Total Reflux Mode

After 10 cycles in total reflux modes, the system reaches steady state condition in its gas compositions within each column for the relevant initialization point mirroring operational characteristics in the EU-DEMO fuel cycle operation. In contrast to the process temperature and pressure swings, the gas composition require more cycles in total reflux operation to run in steady state and are therefore used as criteria to define completed process settling. As can be seen in the plot of the establishing gas phase composition of homo-isotopologue species at the end of each column given in Figure 6.1, more cycles in total reflux mode only increase the necessary time for simulation. The corresponding profiles for hetero-isotopologue compositions are presented in Figure C.3 in the appendix.

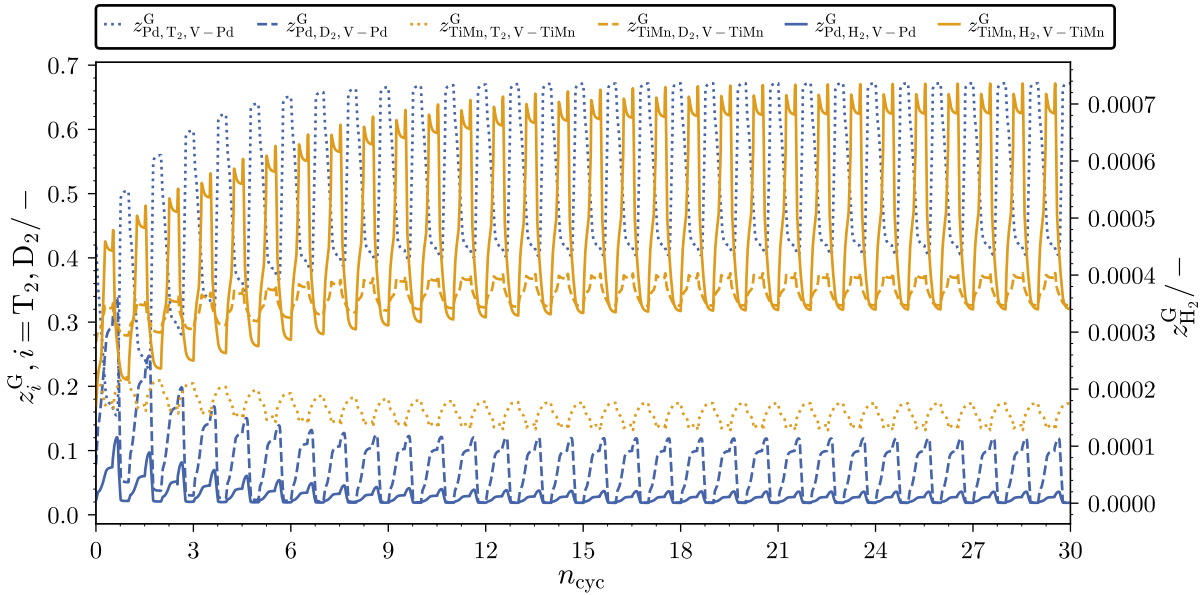


Figure 6.1: Establishing composition of homo-isotopologues T_2 , D_2 and H_2 in the gas phase at the extraction port of the Pd and TiMn column in dependence of the number of performed cycles in total reflux mode. Corresponding hetero-isotopologue composition profiles are shown in Figure C.3 in the appendix. Compositions run into steady state after ~ 10 closed cycles.

Using the establishing hetero-isotopologue gas compositions shown in Figure 6.1 and C.3, the abundances of each isotope H, D and T is calculated by a atomic balance. The resulting protium and tritium fractions at each columns end and the corresponding

maximum enrichment obtained in total reflux mode are summarized in Table 6.3.

Table 6.3: Calculated protium and tritium fractions from atomic balances of the establishing hetero-isotopologue composition in steady state at the extraction ports of the Pd and TiMn column for total reflux operation. Obtained values for enrichment and depletion are related to a feed composition of $z_{\text{feed},T_2}^G = z_{\text{feed},D_2}^G = 0.495$ and $z_{\text{feed},H_2}^G = 0.01$.

Column	z_T^G	z_H^G	Enrichment (E) or Depletion (D) in %	
			T_2	H_2
Pd	0.655	0.0048	32.4 (E)	52 (D)
TiMn	0.4	0.0183	19.2 (D)	83.5 (E)

While the protium content is depleted by 52 % at the extraction port of the Pd column (V-Pd), an enrichment in protium at V-TiMn of 83.5 % is observed, demonstrating the separation capability of the process.

However, in open cycle operation, these enrichments will decrease during withdrawal, due to the gas composition profile present in each column, thus the reported values reflect the maximum reachable purification. Also the re-establishing of the gas profile after each sampling reduces the obtainable enrichments. First, the composition change affects the establishing equilibria and second, due to the repeated feed of H_2 by the feed stream, the composition in the lattice and the gas phase within the columns adjusts. Thus, a new steady state establishes, if the extracted amount allows for a new operation point. These are discussed in detail in Subsection 6.3.2.

The selected heating times of 400 s are sufficient to reach the set-point temperature amplitudes for each temperature swing when running through all process steps (heating and exchange) as visible in Figure 6.3. During absorption phase, i.e., at low temperature level, temperature peaks are obtained, which are caused by the exothermic hydrogenation reaction. In addition, the reaction front progressing through the column is observable by the time-shift between the T profiles calculated at the different valve positions.

The process pressures alternate between absorption and desorption pressures for both columns (c.f. Fig. 6.4). The pressures presented refer to the segments of extraction at each column's end, the exchange node and in the column's mid respectively. During heating and exchange, the gas flows through the column, marked by a pressure distribution caused by the permeation characteristics of the packing. At the exchange point, instantaneous pressure equilibration is observed as the exchange valve or rather orifice shows a less permeation resistance than the bed. A minimum pressure of 69 mbar and a maximum pressure of 2000 mbar establishes, fulfilling the requirements of IRPR operation (c.f. Sec. 1.2) In contrast to that, maximum desorption pressures in the Pd column of

5500 mbar establish in a TCAP scenario [116], while the PFR column pressure alternates between 1200 to 2100 mbar [35].

From Figure 6.2 follows, that the whole reversible capacity of Pd is used during the alternation of absorption and desorption phase (plateau-region extends from $c = 0.1$ to ~ 0.65), while $\text{TiMn}_{1.5,\text{mod}}$ is loaded up to $c = 0.8$, which is a concentration already located at the beginning of the β -phase and de-loaded to $c = 0.25$, which is the transition zone to the α -phase. The latter is unavoidable, due to the higher absorption pressure of $\text{TiMn}_{1.5,\text{mod}}$ in contrast to Pd. Both materials are continuously charged and de-loaded, supported by the the partner column in contrary sorption phase. Therefore, no sudden jumps in the concentration occur, which were observed for HESTIA simulations when gas exchange was triggered by opening the exchange valve (c.f. Fig. 5.14). Since almost the whole reversible capacities of both materials are used, the material amounts are well adapted to each other.

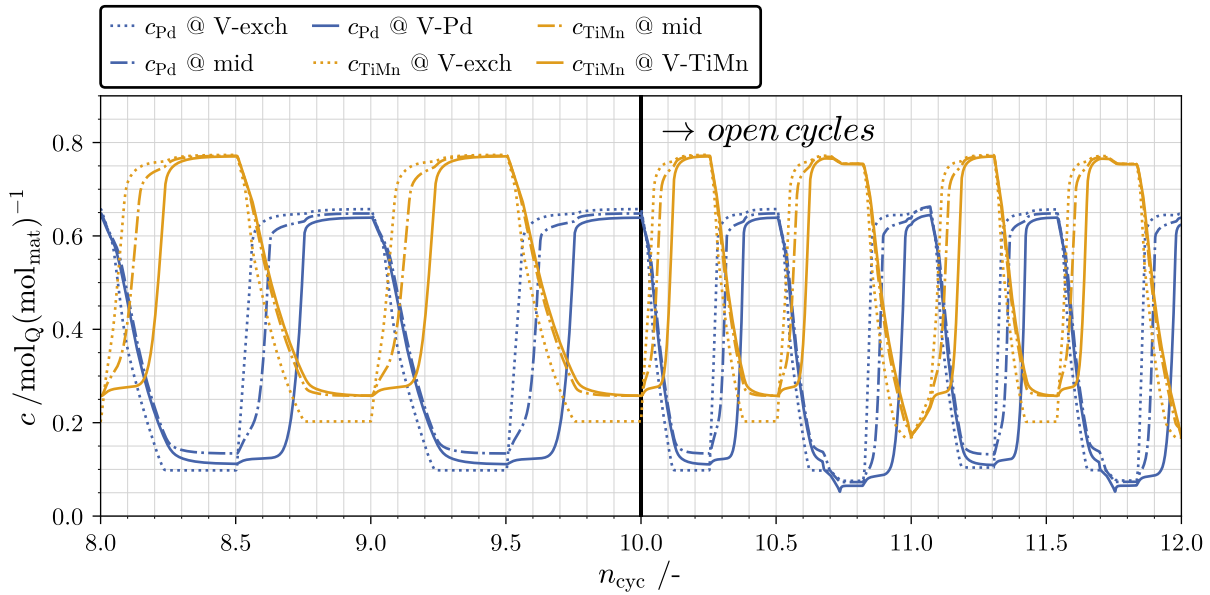


Figure 6.2: Establishing concentration profiles of absorbed hydrogen in the metal lattice at different locations within each absorption columns during IRPR operation. After 10 cycles in total reflux mode, open cycles are tolerated, extracting 10 % of the total column inventory.

Steady State for Open Cycle Operation

To evaluate the establishing operational process parameters in the open cycle operation, the simulation case of 10 % product extraction of the total inventory for zero additional closed cycles is presented and discussed. Concerning the establishing temperature and pressure profiles during operation, this exemplary case sufficiently represents the larger extraction amounts and further closed cycle combinations. The revealing impact of additional closed cycles and variation of the total extracted amount on the product composi-

tion is discussed in Subsection 6.3.2.

The open cycle operation does not impact the establishing temperature profiles, as visualised in Figure 6.3 for $n_{cyc} > 10$. Still the process times given for heating are sufficient to allow for temperature alternation between the set-point temperature amplitudes. During extraction, the temperature simulated at extraction port only slightly decreases due to the heat consumption of hydrogen release.

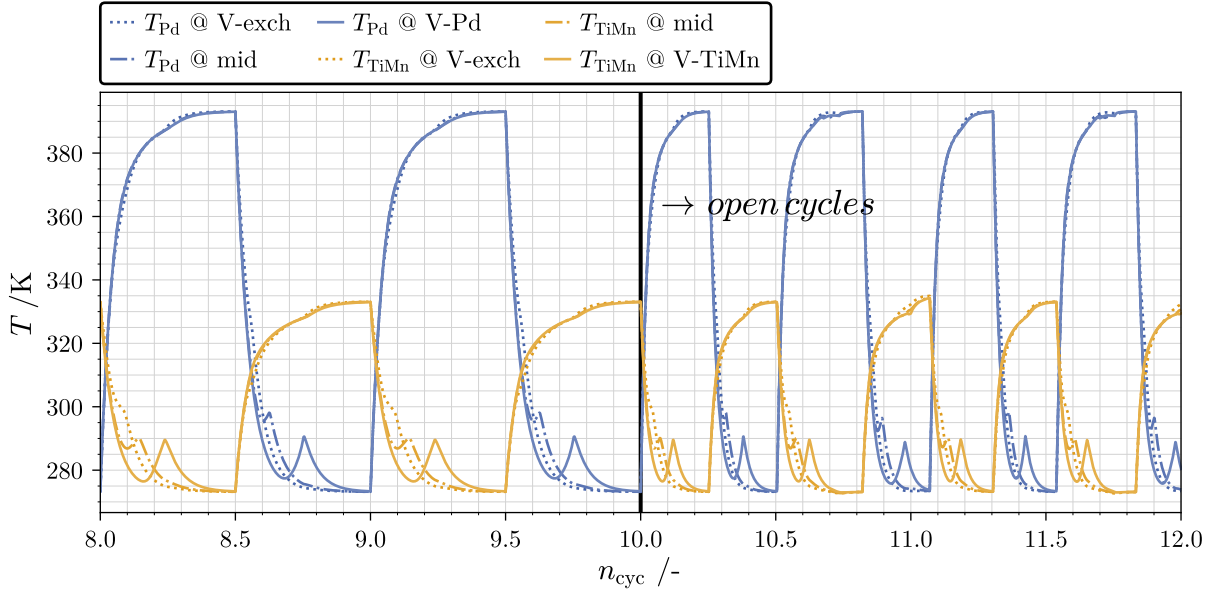


Figure 6.3: Simulated temperature profiles at different locations within the palladium and the TiMn column in dependence of the performed process cycles. After 10 cycles in total reflux mode, open cycles are tolerated, extracting 10 % of the the total column inventory during sampling.

The establishing pressure profiles are shown in Figure 6.4. The highest pressures occur when the Pd column is fed by the Q_2 stream of the exhaust processing system, leading to a maximum pressure of 2600 mbar in the middle of the Pd column (location of feed port). Since pressure plateaus establish, the heating and exchange times are considered sufficient to allow for equilibration before temperature switch or extraction is triggered. At V-Pd the pressure is around 1800 mbar and decreases to 380 mbar during sampling, leading to a mean extraction pressure of 1090 mbar over the sampling time, which fulfils the target pressure of the gas distribution vessel (c.f. Subsec. 6.2.2). After the exchange time given for equilibration with the TiMn partner column, the pressure rises to 1000 mbar, as further Q_2 is released from the Pd lattice according to the equilibrium constitution.

During product extraction of the TiMn column the pressure decreases from 1400 mbar to 990 mbar at the respective port (V-TiMn). This decrease is lower in comparison to the extraction pressure of the Pd column, as only 15 % of the total extraction amount is withdrawn from the TiMn column. Also this pressure reflects the necessary value of the downstream unit, i.e., the isotope separation system. After completed $TiMn_{1.5,mod}$ prod-

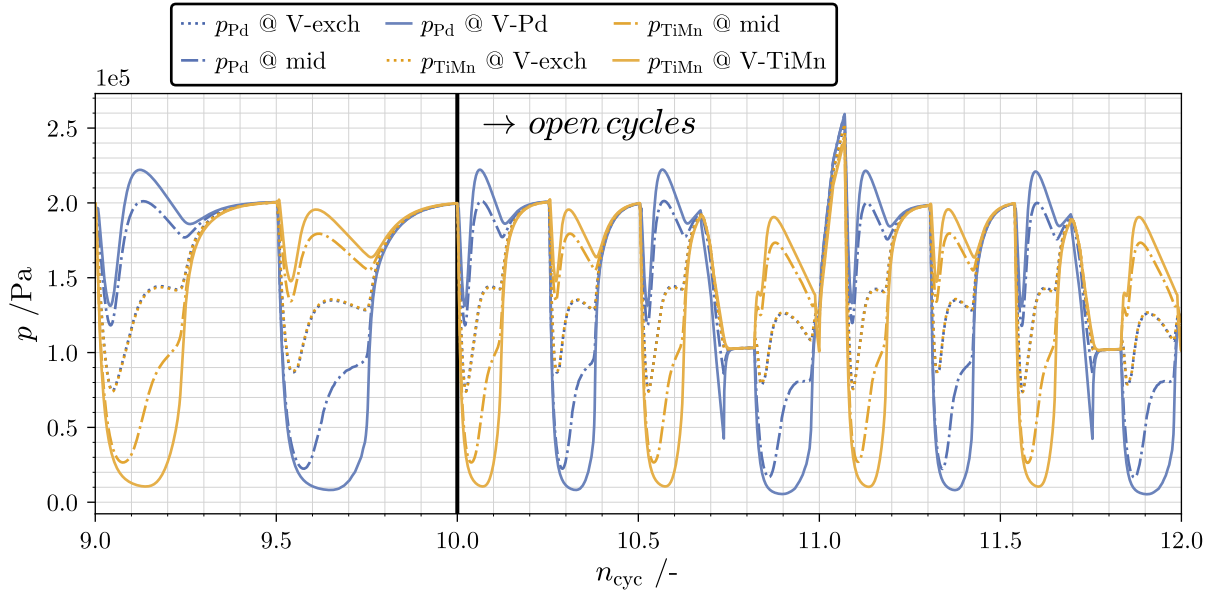


Figure 6.4: Simulated pressure profiles at different locations within the palladium and the TiMn column in dependence of the performed process cycles. After 10 cycles in total reflux mode, open cycles are tolerated, extracting 10 % of the the total column inventory during sampling. At $n_{CC}=11$ a pressure increase caused by feeding is observable, while the pressure decreases as consequence of the product withdrawal are visible at $n_{CC} \approx 10.7$ (Pd) and $n_{CC} \approx 10.95$ (TiMn).

uct extraction, the withdrawn Q_2 amount is immediately replaced by fresh feed, therefore no equilibration plateau is visible.

Finally, as described for the steady state of total reflux operation, the travelling of a pressure front through the column can be observed by the shown profiles for the three different depicted nodes located in the columns. This is caused by the utilization of elongated columns, the time for completed flow through is impacted by the determined permeation of a packed metal hydride column. Since no drifts in the alternating pressure amplitudes are observed, a new steady state condition has settled which reflects a stable operation point.

In Figure 6.5 the Q_2 inventories over the repeated process cycles are distinguished for each column and both phases, i.e., gas and solid phase. The inventories are related to the total inventory processed, which is 1.82 mol (c.f. Tab. C.4). During total reflux operation, no inventory is withdrawn, thus $N_{\text{tot}}/N_{\text{max}}$ remains 1. During open cycle operation ($n_{\text{cyc}} > 10$), the inventory is reduced by 10 % in each completed cycle, whereby 8.5 % are withdrawn from the Pd column and the remaining 1.5 % are extracted from the TiMn column respectively. During processing most of the Q_2 is bound in the solid phase of either the Pd or the $\text{TiMn}_{1.5,\text{mod}}$ lattice. In fact, less than 1 % of the inventory is present in the gas phase during the whole processing. 86 % of the inventory is absorbed in the TiMn column in its absorption phase. Thus, a non-processed residual Q_2 inventory of

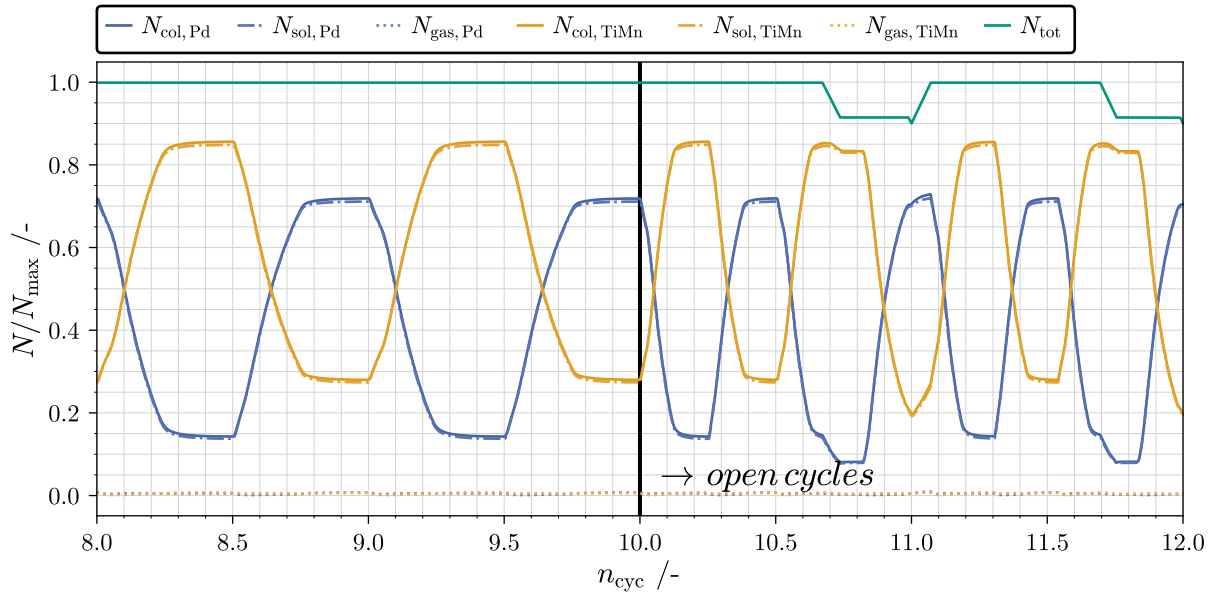


Figure 6.5: Molar Q_2 inventories splitting in gas and solid phase in the Pd and TiMn column in dependence of the cycle number. After 10 cycles in total reflux mode, open cycles are tolerated, extracting 10 % of the the total column inventory during sampling.

14% remains in the Pd column. In contrast, the Pd column absorbs 71% of the total inventory in absorption phase, leaving a non-processed Q_2 inventory of 29% in the $TiMn_{1.5,mod}$ lattice. In comparison to a TCAP system, where the second column (PFR) does not absorb hydrogen and is able to contain half of hydrogen amount storable in the Pd column [54], the residual inventory in the Pd lattice is lowered by 72% when using the TiMn column. Thus, the residual hydrogen which does not contribute to separation is significantly reduced. This supports the optimization potential of the TSA process by utilizing a second active absorption column which further empties the partner column in desorption phase due to its capability to pump.

Figure 6.6 presents the impact of open cycle operation on the gas phase composition. Due to the repeated feed of fuel containing H_2 , the composition of isotopes in the lattices and gas phases shifts from the initialization values. The repeated withdrawal of enriched product fractions lowers the purification of the non-favored isotope species at the column's ends. However, although the compositions slightly shifts, it can be seen that a new steady state establishes after 10 open cycles. Thus, the semi-continuous process allows for a stable operation point. Also Heung et al. utilized 10 cycles in their TCAP experiments to let the system settle after a change of process parameters [35]. These observations give an idea of the necessary system reaction time to adapt to a sudden operational change (step response). The obtained enrichments are dependent of the extracted product amounts as well as performed additional closed cycles, and are discussed in the next section for each investigated operation scenario.

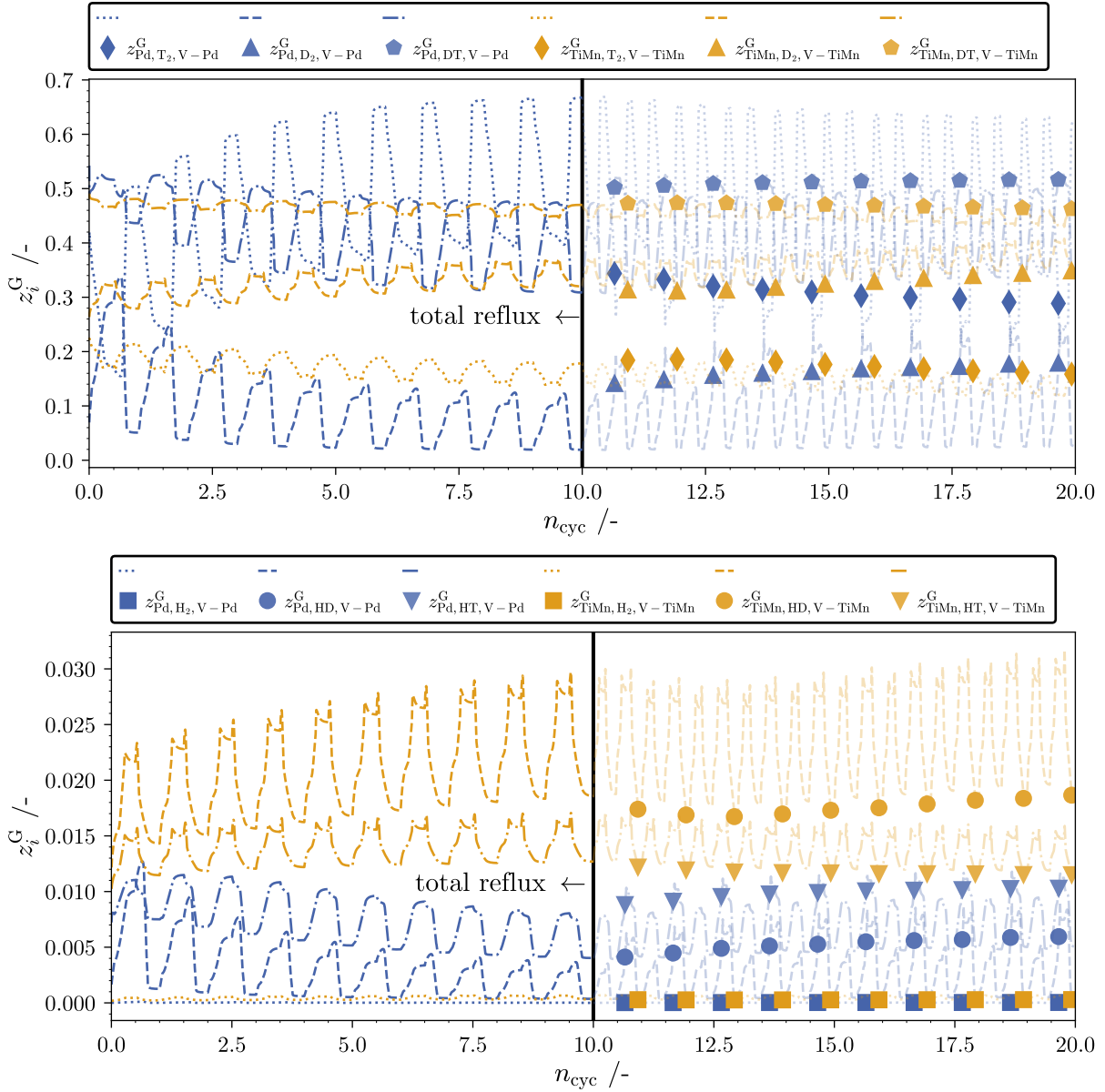


Figure 6.6: Establishing composition of T_2 , D_2 and DT (top) and H_2 , HD and HT (bottom) in the gas phase at the extraction port of the Pd and TiMn column in dependence of the number of performed cycles. After 10 cycles the operation in total reflux mode is switched to open cycles. Markers refer to the integral product composition obtained during withdrawal. Translucent lines indicate the adapting compositions during cycling in open cycles.

6.3.2 Enrichments for Relevant Operation Scenarios

To identify the a promising operation routine for a IRPR CMH-TSA application, the extracted product amount and the number of additional closed cycles were varied and the impact on the obtained product composition evaluated. These purities and enrichments in combination with the resulting column throughput serve in Section 6.4 to determine the yield of protium, i.e., the counteracting bleed stream provided by the IRPR system,

and from this the tolerable protium source term.

Impact of Extracted Product Amount on Product Compositions

The atomic composition of both product streams was calculated by determining the integral product composition at each extraction port (V-Pd and V-TiMn) over the sampling time. In Figure 6.7 the obtained atomic tritium fraction $z_{T,Pd}^G$ of the Pd column product and the atomic protium fraction $z_{H,TiMn}^G$ of the TiMn column product are related to the amount of extraction $\frac{N_{extr}}{N_{tot}}$ for no additional closed cycle ($n_{CC} = 0$). These fractions represent the valuable products from these product streams, which shall be maximized by the operation routine.

With increasing withdrawal the abundance of the valuable product reduces in the product streams. While for an extraction amount of 5 % from the total inventory the Pd product stream consists of 60 % tritium, $z_{T,Pd}^G$ reduces to 0.52 for an amount of 15 %. For comparison, in total reflux mode an molar tritium fraction of 0.655 revealed. Thus, the achievable product composition is reduced when open cycles are operated. The same decrease can be observed for the protium value product. Here, the protium proportion equals 1.6 % ($\frac{N_{extr}}{N_{tot}} = 5\%$) and lowers to 1.4 % ($\frac{N_{extr}}{N_{tot}} = 15\%$), while 1.83 % were reached in total reflux operation. As expected, the more product is extracted from the column inventories, the lower the enrichment in the targeted isotopes. However, this is a trade-off, as lower extraction amounts refers to higher numbers of parallel CMH-TSA units to process the targeted IRPR system throughput (c.f. Fig. 6.9).

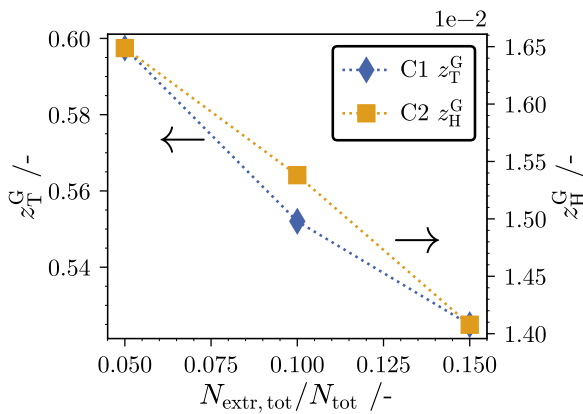


Figure 6.7: Establishing atomic fractions of value products (C1 = T, C2 = H) in dependence of the extraction amount referred to the total inventory for no additional closed cycle n_{CC} .

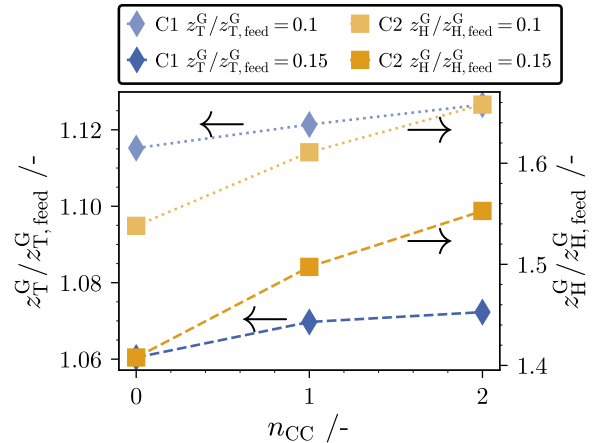


Figure 6.8: Obtained enrichment of value products related to the feed composition ($z_{T,feed}^G = z_{D,feed}^G = 0.495$ and $z_{H,feed}^G = 0.01$) in dependence of the number of additional closed cycles for 10 % and 15 % extraction of the total inventory.

Impact of Additional Closed Cycles on Value Product Enrichment

The obtained enrichments of the value products in relation to the feed composition for the investigated process routines are given in Figure 6.8. For a feed composition of $z_{\text{T}_2, \text{feed}}^{\text{G}} = z_{\text{D}_2, \text{feed}}^{\text{G}} = 0.495$ and $z_{\text{H}_2, \text{feed}}^{\text{G}} = 0.01$, the enrichment in H_2 in the TiMn column product increases from 54 % ($n_{\text{CC}} = 0$, 10 % extraction) to 65.8 % ($n_{\text{CC}} = 2$, 10 % extraction). The enrichments are reduced for $\frac{N_{\text{extr}}}{N_{\text{tot}}} = 15$ %, reading 40.8 % ($n_{\text{CC}} = 0$) to 55.3 % ($n_{\text{CC}} = 2$). Since a larger product amount is extracted from the Pd column (c.f. Subsec. 6.2.2), the obtained enrichments in T_2 are lower in comparison. However, still an enrichment of 11.5 % ($n_{\text{CC}} = 0$) to 12.7 % ($n_{\text{CC}} = 2$) for 10 % extraction is obtained.

The impact of additional closed cycles is intended to counteract the reduced enrichments of higher extraction amounts, and is also evaluated by Figure 6.8. The highest increase is observed in the enrichment of $z_{\text{H}, \text{TiMn}}^{\text{G}}$. Here, each additional n_{CC} leads to around 4.7 % larger enrichments (TiMn) and 3.6 % further depletion (Pd). However, this effect reduces for further cycles. For the other species the impact is lower, i.e., $z_{\text{T}, \text{Pd}}^{\text{G}}$ is enriched by only 0.5 % and depleted by 2 % in the $\text{TiMn}_{1.5, \text{mod}}$ product stream.

In regard to the increase of required number of parallel column systems this slight impact on the enrichment and depletion is strongly reduced. To enable one further additional closed cycle, the column number increases from 69 to 102 (10 % withdrawal) up to 134 for $n_{\text{CC}} = 2$ (c.f. Fig. 6.9). For 15 % extraction, the column numbers increase from 46 ($n_{\text{CC}} = 0$), to 68 ($n_{\text{CC}} = 1$) up to 89 ($n_{\text{CC}} = 2$). It follows, that the profit in purification per n_{CC} does not compensate the disadvantage of the rise in necessary column pairs to counteract the reduced throughput processable by a CMH-TSA unit as the sensitivity of product composition is not distinct enough towards the number of n_{CC} . This observation is further discussed in Section 6.4. Thus a process operation without additional closed cycles is suggested. It should be noted, that the here presented enrichments are correlated to atomic compositions reflecting the abundance of each isotope within the hetero-molecular product constitution of six isotopologue species. The discussed H_2 and T_2 enrichments should not be misunderstood for complete separation into homo-isotopologue, as realized in the isotope separation system.

6.4 Required IRPR System Size

The resulting TiMn column product compositions, which are dependent on the operation routine as discussed in Subsection 6.3.2, are used to determine the the time-averaged stripped H_2 stream per CMH-TSA unit. This stream equals the yield of protium product, which is discharged as bleed stream to the OUTL. In addition, the obtained H_2 protium

streams extracted per CMH-TSA base unit allow for determining the required number of parallel column pairs to counteract the protium source term, thus to size the IRPR system for its separation task. For the EU-DEMO fuel cycle, up to the current point of knowledge, the H_2 source term entering the fuel cycle due to outgassing from the vacuum vessel is not known and estimated to be $0.1 \text{ Pam}^3/\text{s}$, serving for reference [18, 22]. In addition, as preliminary design point a throughput of $11 \text{ Pam}^3/\text{s}$ is targeted for the IRPR system.

Figure 6.9 summarizes the revealing protium bleed stream per column pair for each investigated operation, i.e., varying extraction amounts and additional closed cycles, and correlates them to the required number of column pairs. The largest protium bleed stream per column unit is obtained from 15% extraction and zero additional closed cycles, reading $5.2 \cdot 10^{-4} \text{ Pam}^3/\text{s}$. In comparison, the lowest extractable bleed stream per CMH-TSA unit of $2.2 \cdot 10^{-4} \text{ Pam}^3/\text{s}$ follows from an operation of zero additional closed cycle and 5% extraction amount.

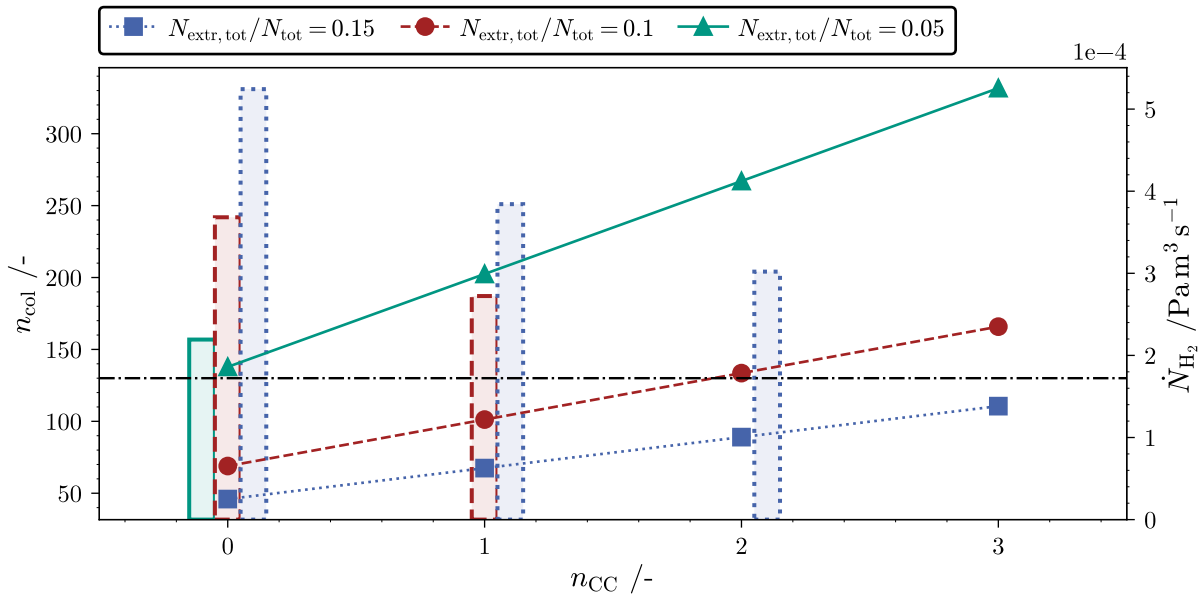


Figure 6.9: Obtained protium bleed stream $\dot{N}_{H_2}$ per CMH-TSA base unit for varying extraction amounts and numbers of closed cycle in relation to the required of number of column pairs for a IRPR system throughput of $11 \text{ Pam}^3/\text{s}$. Dashed-dotted line refer to the defined upper column pair limit of 130 parallel systems.

From this evaluation directly follows, that the number of necessary column pairs quickly out-range a reasonable number of parallel systems. For economical reasons, column numbers above 130 required for processing $11 \text{ Pam}^3/\text{s}$ were not further considered, as those demand a Pd amount of about 55 kg (1 kg Pd costs around 30kUS\$ [117]). Therefore, resulting bleed streams for extraction amounts $< 15\%$ of the total inventory are only determined for column numbers < 130 pairs.

The total H_2 bleed stream discharged by the IRPR system follows from the number of parallel columns and the H_2 bleed stream extracted per column pair. Table 6.4 summarizes the resulting IRPR system sizes for the analysed operation routines. Two separation task scenarios and the corresponding required IRPR size are compared. The tolerable protium source term, which can be counteracted by an IRPR system for the reference design point, i.e., an IRPR system throughput of $11 \text{ Pam}^3/\text{s}$, and the required IRPR system size to counteract the assumed protium source term of $0.1 \text{ Pam}^3/\text{s}$.

Table 6.4: Overview of required parallel column systems for processing an IRPR throughput of $11 \text{ Pam}^3/\text{s}$ in comparison to revealing dimensions necessary to completely counteract a protium source term of $0.1 \text{ Pam}^3/\text{s}$ for the investigated operation routines.

		$\dot{N}_{\text{IRPR}} \stackrel{!}{=} 11 \text{ Pam}^3/\text{s}$		$\dot{N}_{\text{source}, H_2} \stackrel{!}{=} 0.1 \text{ Pam}^3/\text{s}$		
$\frac{N_{\text{extr}}}{N_{\text{tot}}}$	n_{CC}	n_{col}	max. $\dot{N}_{\text{source}, H_2}$	n_{col}	min. $\dot{N}_{\text{IRPR}}$	$\dot{N}_{\text{IRPR} \rightarrow \text{OUTL}}$
0.05	0	138	0.030	456	36.4	5.5
0.1	0	69	0.025	272	43.3	6.5
0.1	1	102	0.028	367	39.9	6.0
0.15	0	46	0.024	191	45.7	6.9
0.15	1	68	0.026	260	42.4	6.4
0.15	2	89	0.027	331	40.9	6.1
0.15 (cold)	0	46	0.044	104	24.9	3.7

The tolerable H_2 source term, which can be counteracted by the given IPRR throughput of $11 \text{ Pam}^3/\text{s}$, varies from 0.024 to $0.0303 \text{ Pam}^3/\text{s}$. However, the required number column pairs differs significantly. The lowest column pair number of 46 corresponds to a tolerable source term of $0.024 \text{ Pam}^3/\text{s}$, while the highest tolerable source term is counteracted by operating 138 CMH-TSA units. As concluded in Subsection 6.3.2, further additional closed cycles do not significantly increase the enrichment, therefore the tolerable protium source term does not largely differ for equal extraction amounts and varied numbers of closed cycles. By analyzing the H_2 source terms, which can be counteracted, it becomes clear, that the IRPR system throughput of $11 \text{ Pam}^3/\text{s}$ is too low to provide the required H_2 bleed stream. Thus, the separation efficiency of the system was overestimated.

For completely counteracting the source term of $0.1 \text{ Pam}^3/\text{s}$, the IRPR system throughput has to be increased to up to $45.7 \text{ Pam}^3/\text{s}$, depending on the operation scenario (c.f. Tab. 6.4). In general, a maximum process stream of $\sim 20\%$ of the torus throughput, which equals $86 \text{ Pam}^3/\text{s}$ to the current EU-DEMO design point [18], can be routed to the INTL if necessary. For the reference design point, the remaining $75 \text{ Pam}^3/\text{s}$ were bypassing the IRPR system.

From the resulting IRPR system size can be concluded, that the TSA process is closely pushed to its limits by the very demanding separation task of the EU-DEMO fusion fuel cycle. With each operating column the system inventory of T_2 increases. For completely counteracting a source term of $0.1 \text{ Pam}^3/\text{s}$, a T_2 inventory of $N_{T_2} = (1.8 - 0.27) \text{ mol} \cdot 191 \text{ columns} \cdot z_{T_2, \text{feed}}^G = 144.7 \text{ mol} \hat{=} m_{T_2} = 868 \text{ g}$ for the IRPR system follows. However, for this throughput the inventory for all hydrogen isotope separation technologies is large. For comparison: The cryo distillation test facility TSTA developed in Los Alamos Scientific Laboratory processes a mixed isotopologue feed stream of $1.9 \text{ Pam}^3/\text{s}$ composed of $z_{T_2, \text{feed}}^G = z_{D_2, \text{feed}}^G = 0.495$ and $z_{H_2, \text{feed}}^G = 0.01$ already has a T_2 inventory of 102.2 g [118, 119]. A TSA system processing the same feed flow rate requires 8 column pairs and operates with a T_2 inventory of 36.4 g . Thus, it can be assumed, that for the required IRPR throughput a CMH-TSA technology is still beneficial compared to cryo distillation.

As the required number of parallel column pairs is high and comes along with high tritium inventory, the process operation is further adapted, taking advantage of the continuous gas interaction between the separation columns. If product streams are not withdrawn by the column in desorption phase, but instead in absorption phase, a higher separation factor α can be exploited, which increases for lower temperatures (Eq. (2.7)), thus higher product enrichment might be reached. In this scenario, the necessary pressure to enable product extraction is provided by the continuous equilibration to the partner column in desorption phase. In contrast, during isolated absorption phase, the Pd column in a TCAP scenario exhibits pressures of several mbar [35], which are not sufficient for product extraction. The impact of this operation adaption and the evaluation towards system integration is discussed in Subsection 6.4.1.

6.4.1 Exploiting Product Extraction from Cooled Column

This subsection introduces a further concept of an CMH-TSA process, which operates with two active absorption columns under continuous gas exchange. Hereby, the product sampling is realized during the absorption phase of each column, thus at its low temperature set-point. This aims for exploiting higher separation factors.

A simulation was performed, using the same initialization, parameters and process times as given in Table C.4 in the appendix, but using an adapted routine which switches step 5 and 7 (c.f. Tab. 6.1). Restrictive for this operation variant are the establishing pressures during extraction, which are limited by the request of system integration, but are considered to be reduced due to absorption conditions. However, when evaluating the establishing pressure profiles shown in Figure C.4, it can be concluded, that the reduced process pressures fulfil this criteria.

Figure 6.10 shows the resulting gas phase compositions for this process variant. As in the previous operation cases (c.f. Subsec. 6.3.1), first the system is allowed to run into steady state after 10 cycles in total reflux mode, then open cycles are alternated. To enable a direct comparison, the most promising operation scenario identified in Table 6.4 is studied, i.e., $\frac{N_{\text{extr}}}{N_{\text{tot}}} = 15\%$ without further closed cycles. A new operation point establishes, as the composition of isotopes within the lattice has to re-adapt to the repeated feed and extracting. However, the necessary number of cycles to run into a new steady operation point are larger than in the beforehand discussed operation modes. In addition, it is noticeable, that especially the D_2 and DT molar fractions enriches at both extraction ports.

The effect of extracting at low temperatures reveals in the obtained enrichment. The product stream of the TiMn column is enriched by 178 % in H_2 , while the Pd column product stream is depleted by 53.5 %. Transferring this result to the stripped H_2 stream, a source term of $0.044 \text{ Pam}^3/\text{s}$ can be tolerated (for a total IRPR throughput of $11 \text{ Pam}^3/\text{s}$) while operating 46 parallel column pairs. This is 84 % higher than the tolerable stream for product extraction during desorption phase. In other words, to completely counteract the currently assumed H_2 source term of $0.1 \text{ Pam}^3/\text{s}$, 104 column pairs are required (vs. 191 for desorption phase extraction). Still this number is very elevated concerning the required amount of Pd, however, the throughput performance increase is remarkable. In addition, the T_2 inventory follows from $N_{\text{T}_2} = (1.8 - 0.27) \text{ mol} \cdot 104 \text{ columns} \cdot z_{\text{T}_2, \text{feed}}^{\text{G}} = 80.3 \text{ mol} \hat{=} m_{\text{T}_2} = 481.7 \text{ g}$, which is significant lower than obtained from the configuration exploiting product extraction in desorption phase.

This process variant seems very promising and should be investigated closer in future and tested in a relevant lab-scale column system. Especially the distribution of DT and D_2 has to be confirmed and the increased cycle number to settle for a new operation point. To the best of the author's knowledge, this kind of CMH-TSA process operation has not been investigated so far. However, it not only transforms a gas chromatographic process into a semi-continuous process, it also offers the possibility to completely utilize the separation potential of the absorption materials during cold temperatures, where the separation factor reaches its maximum. This optimization is only realizable in a CMH-TSA process operation with two active separation columns.

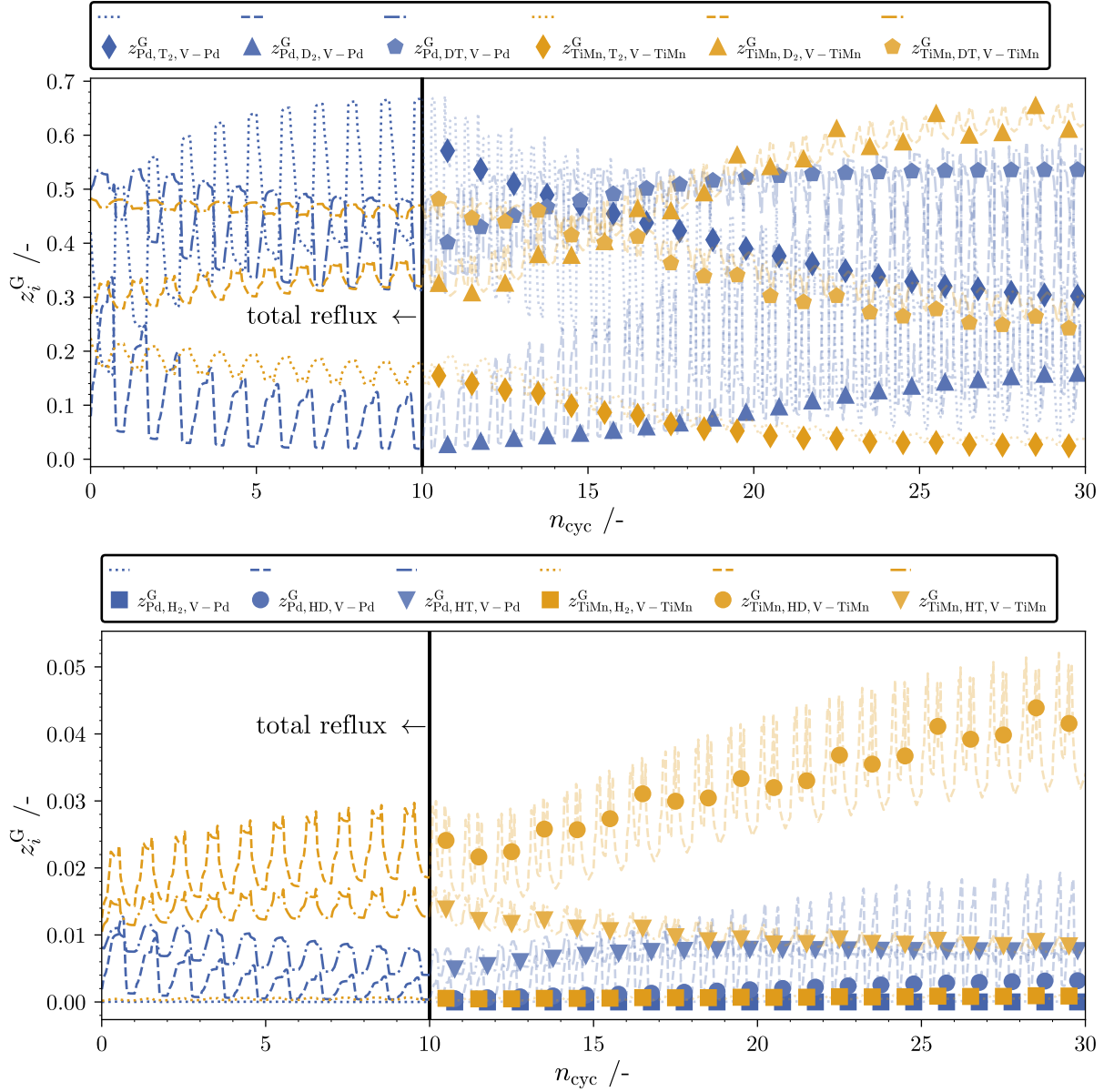


Figure 6.10: Establishing composition of T_2 , D_2 and DT (top) and H_2 , HD and HT (bottom) in the gas phase at the extraction port of the Pd and TiMn column in dependence of the number of performed cycles. After 10 cycles the operation in total reflux mode is switched to open cycles. Product extraction is performed in absorption phase (*cold extraction*). Markers refer to the averaged product composition. Translucent lines indicate the adapting compositions during cycling in open cycles.

6.5 Conclusions of CMH-TSA Technology for EU-DEMO IRPR

In this chapter the developed CMH-TSA process was investigated concerning its large scale behavior and capability to serve as technology for the IRPR system in the EU-DEMO fuel cycle. For this, the CMH-TSA model was used to simulate the separation and process performance of a base CMH-TSA column pair, exploring different operation scenarios.

First, an optimized operation variant was proposed, which exploits the gas transfer interactions of two coupled active separation columns and allows for increased system throughput. The simulated profiles of the establishing operation parameters verified a distinct enrichment of the valuable products in each product stream. In addition, no cryogenic temperatures are required and desorption temperatures can be chosen moderate. This means the delta of the temperature amplitudes is reduced, causing shorter heating times, leading to faster cycling times.

The obtained process pressure are lower than 2500 mbar, thus in agreement with the targeted pressure range. In addition, the required product pressures to allow for system integration are ensured by the chosen operational temperatures.

The process cycling time is shorter than the residence time of the inner loop of the fusion fuel cycle. It has been shown, that the impact of additional closed cycles after product extraction to reach higher product enrichments is rather limited. Instead, it reveals, that the smallest number of parallel column pairs to counteract protium built-up in the recycled fuel is reached by extracting 15 % of the total column inventory without additional closed cycles. In addition, the potential of product extraction in absorption phase (*cold extraction*) was identified, as it offers a promising optimized process operation to significantly reduce the necessary parallel column number, since separation factors are increased at low temperatures.

It became clear, that the separation task demanded by a fusion fuel cycle is very challenging for CMH-TSA technology, despite the optimization progress. To completely counteract the protium built-up, 104 parallel column pairs are necessary (desorption phase extraction) which refers to a total IRPR throughput of $24.9 \text{ Pam}^3/\text{s}$ instead of the pre-assumed $11 \text{ Pam}^3/\text{s}$. The required number of parallel columns exhibits an integral tritium inventory of approximately 481.7 g, which is lower than a corresponding cryo distillation system operates at a similar throughput (c.f. Sec. 6.4). Alternatively, a H_2 source term of $0.044 \text{ Pam}^3/\text{s}$ can be tolerated if the IRPR throughput is fixed to $11 \text{ Pam}^3/\text{s}$.

The results of the simulated cases offer three possibilities: Either a higher H_2 protium content is tolerated in the fuel or an increased IRPR throughput is accepted. The last option is to increase the outer fuel cycle loop loading. Whether, from an economic point

of view, the operation of a large IRPR or a larger cryo distillation system is the optimum, i.e., energy consumption and investment cost for Pd, outreaches the scope of this work, but is strongly suggested to be evaluated in future.

A final recommendation is to spent further research to optimize the $\text{TiMn}_{1.5,\text{mod}}$ system concerning its separation factor. Due to the proven large separation efficiency of Pd, the overall process enrichment capability is expected to be limited by $\text{TiMn}_{1.5,\text{mod}}$. Furthermore it should be noted, that all thoroughly performed simulative studies do not replace experimental investigation under tritium conditions to verify the real system behavior.

The simulations verified that the CMH-TSA process is optimized by the introduction of a second active separation column, showing an opposite isotope affinity than Pd, which was stated by hypothesis 2. A second active separation column enables further operation variants, which increase the system throughput, allowing CMH-TSA to be capable for large scale separation process applications, which supports hypothesis 4. However, in regard to the challenging separation task of the EU-DEMO fusion fuel cycle, the developed CMH-TSA process is reaching its limits. In general, the CMH-TSA process is capable to fulfil the separation task while complying with all process requirements concerning its operational parameters and within the available throughput range of the INTL. However, this capability is accompanied by high costs of absorption materials, numbers of parallel system and therefore tritium inventory, which is caused by the semi-continuous operation. Nevertheless, for all fusion machines investigated and under development, which consider a TCAP within their fuel cycle architecture, i.e., LIFE, ARC, STEP or CFETR [120, 121, 122, 123], the presented CMH-TSA process is suggested as versatile optimized technology.

Chapter 7

Summary and Outlook

The fuel cycle of the envisioned European Demonstration Power Plant (EU-DEMO) foresees an Isotope Rebalancing and Protium Removal (IRPR) system to re-establish the optimal fuel educt composition and to strip-off contained protium which unavoidable built-up within the recycled fuel stream. A temperature swing absorption (TSA) process is the primary technology candidate for the combined hydrogen isotope separation task to be realized in the IRPR unit (hypothesis H1). The driving research hypothesis H2 states that the separation efficiencies and throughputs of established TSA processes, like the Thermal Cycling Absorption process (TCAP), which is set-up by a separating palladium column and an inert plug flow reverser column, are optimized by the introduction of a second packed separation column. It is filled with an absorption material showing an opposite isotope effect on the hydride formation than palladium. This work focussed on the development of the coupled inverse and normal metal hydride reaction temperature swing absorption (CMH-TSA) process which exploits opposite isotope dependent metal hydride formation of two coupled absorption columns.

First, material studies of customized Titan-alloys allowed for analysing the isotope dependent metal-hydrogen-characteristics using a Sieverts' Apparatus. These measurements proven the inverse isotope effect on its hydride formation for the TiMn-alloy $\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.48}\text{Fe}_{0.10}\text{V}_{0.42}$ referred to as $\text{TiMn}_{1.5,\text{mod}}$, which is a derivate of the low temperature hydride storage material Hydralloy C5. A separation factor of 1.6 was identified in the relevant process temperature range. In addition, hydride formation characteristics and kinetics in the relevant CMH-TSA operation range and comparable to the palladium-hydrogen-system were verified, thus H3 - an absorption material having an inverse isotope effect and metal-hydrogen-interactions comparable to Pd exists - was confirmed. This customized material combination of $\text{TiMn}_{1.5,\text{mod}}$ and Pd was used to perform $\text{H}_2\text{-D}_2$ separation experiments in the laboratory set-up HESTIA to investigate various operation scenarios and demonstrate the separation capability. However, a contamination of the

TiMn_{1.5,mod} alloy was verified during these experiments, which occurred in the activation procedure. Furthermore, it did not succeed to sufficiently distribute TiMn_{1.5,mod} over the whole absorption columns length, which leads to inhibition of its separation potential.

Nevertheless, the experimental data of the HESTIA campaign and especially the data collected during material characterization served as input for the developed one dimensional, rate- and physics-based dynamic CMH-TSA model, which serves to support the process design. This model allows for simulation of further operation scenarios and depicts the dynamic interaction of both absorption columns during running through the repeating process scheduling. To the best of the author's knowledge, this model is first of its kind in regard of reflecting the process dynamics of two metallic absorption materials having opposite isotope affinities. Furthermore, the process model was successfully validated by the obtained experimental data and extrapolated to operation under tritium conditions. Using the CMH-TSA model to mimic HESTIA operation, it was possible to verify the contamination of TiMn_{1.5,mod} in HESTIA and its accumulation within the column causing a suppression of the chromatographic effect. On the other side, simulation results of ideal HESTIA behavior demonstrate an enhanced separation efficiency in comparison to a TSA process operating only one separation column. However, repeating separation experiments utilising an optimized TiMn_{1.5,mod} composite material are recommended for future work, for final validation.

A preliminary CMH-TSA design in relevant IRPR EU-DEMO scale was proposed and analysed concerning the establishing operation parameters for different operation variants and schedules. For this, the developed CMH-TSA model served as design tool, allowing for fast design and operation iterations, enabling further process range limitation to relevant operation options.

To realize large scale application and overcome throughput limitations, an optimized process operation variant is suggested, which exploits the the dominant gas chromatographic separation effect and the capability of each column to pump its partner column. This significantly reduces non-processed hydrogen inventory remaining in the metal lattice during desorption. Evaluation of the simulated data demonstrate non-cryogenic process operation at moderate process pressures below 5 bar. In fact, both materials can be operated at 0 °C during absorption phase and 120 °C (Pd) or 60 °C (TiMn_{1.5,mod}) during desorption, while the establishing process pressures reaches a maximum of 2.5 bar. Allowing for continuous gas exchange between the columns reduces the cycling time, pressure peaks and operational temperature amplitude difference, leading to a significant increase of the processable system throughput, while reducing the energy consumption. In addition, exploiting the interactions between both active separation columns enables a product extraction during the absorption phase of each column. This *cold extraction* has the significant advantage of utilising an increased separation factor due to the lower column temperature.

Conceptual simulation revealed sufficient pressures during extraction required for system integration in the overall fuel cycle dynamics.

The preliminary CMH-TSA design suggested has a column geometry of 10 m in length, 10 mm in diameter and 4 mol of active material in each column respectively, allowing for operating a Q_2 inventory of ~ 1.8 mol per CMH-TSA column pair. The necessary scale-up to the IRPR system throughput is reached by parallelization of this base column pair. Estimations by the simulation runs deliver an acceptable protium source term of $0.044 \text{ Pam}^3/\text{s}$ which can be counteracted by this system for the current fuel cycle design point, i.e., an IRPR system throughput of $11 \text{ Pam}^3/\text{s}$. This follows from the obtained enrichment in protium of 178 %. To completely counteract the assumed protium source term of $0.1 \text{ Pam}^3/\text{s}$, a set of 104 column pairs is necessary, which have a T_2 inventory of approx. 481.7 g, showing the demanding separation task of the EU-DEMO fuel cycle. However, a T_2 inventory comparison between a TSA and cryo distillation (CD) system processing equal throughputs and feed compositions showed that CMH-TSA operates with only 35.6 % of the CD T_2 inventory. From these results it is concluded that the CMH-TSA technology is in general capable to fulfil the EU-DEMO separation task, which confirms H1, however, it is not finally answered if an economic operation is possible. Thus, H4 - the CMH-TSA process is such efficient and economical to serve for large scale applications in commercial fusion fuel cycles - is not completely confirmed. However, it can be concluded that all currently developed fusion machines considering a TCAP for isotope separation can be improved by the presented CMH-TSA process.

Future Research Work

After demonstrating the potential of the CMH-TSA process developed in this work, several open points for future investigations and optimizations remain. First of all, further effort should be spent in the material development of $\text{TiMn}_{1.5,\text{mod}}$. This includes the manufacturing of a composite consisting of $\text{TiMn}_{1.5,\text{mod}}$ as active absorption material and an inert structure material to enable a uniform distribution over the whole columns length to reach the full potential of the chromatographic separation effect. This also enhances the gas-solid-interaction and hydride formation reaction. In addition, material investigations focussing on the impact of alloying components on the separation factor offer the potential to identify $\text{TiMn}_{1.5}$ alloy compositions to further increase the process separation efficiency. This allows the full optimization potential of the second active column on the process to be exploited.

To further strengthen the accuracy of the developed CMH-TSA model, additional input data of the material characteristics are of interest. These include more detailed studies on

the absorption kinetics, but especially data of tritium-metal characteristics. The limited data base for the tritium extrapolation utilized in this work causes model inaccuracy. In addition, separation experiments should be performed, exploiting a non-contaminated $\text{TiMn}_{1.5,\text{mod}}$ alloy, to complete the validation of the CMH-TSA model. This in turn allows for more precise design optimizations.

Finally, metal-hydrogen-interactions are strongly related to the system scale, therefore separation experiments in large scale are suggested and currently under development. The DIR integrated Development Platform Karlsruhe (DIPAK) foresees a CMH-TSA facility which has the preliminary design dimensions of a CMH-TSA unit for the IRPR EU-DEMO system. Also, this facility will be optimized concerning the malfunctions of HESTIA, which were identified during the experimental campaigns. This updated facility should be used to investigate the proposed operation variant allowing for continuous gas exchange to verify the increase in system throughput. In addition, real effects during operation and the potential of cold extraction in absorption phase can be investigated. These results will serve as base for an economical evaluation of the CMH-TSA process.

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List of Symbols

Latin Symbols

$\dot{N}$	molar stream	mol(s)^{-1}
$\dot{Q}$	heat flow	J(m)^{-1}
$\dot{S}$	molar absorption or desorption stream	mol(s)^{-1}
$\dot{V}$	volume flow	$\text{m}^3(\text{s})^{-1}$
$\tilde{M}$	molar mass	g(mol)^{-1}
A	area	m^2
a	stoichiometric reaction coefficient	-
A_{jk}	correlation parameter isotopic exchange reaction	-
b	stoichiometric reaction coefficient	-
B_{jk}	correlation parameter isotopic exchange reaction	K
c	atomic hydrogen loading in material	$\text{mol}_Q(\text{mol}_{\text{mat}})^{-1}$
c_{light}	speed of light	m(s)^{-1}
c_p	isobaric heat capacity	J(molK)^{-1}
$c_{\text{SOS},i}$	speed of sound of species i	m(s)^{-1}
D	diameter	m
H	enthalpy	J
h	specific enthalpy	J(mol)^{-1}
hys	hysteresis factor	-
k	permeation coefficient	m^2
k_{CV}	flow coefficient	mol(sPa)^{-1}
k_{heat}	heat transfer coefficient	J(mK)^{-1}
k_p	transport parameter	$(\text{sPa}^2)(\text{K}^{1.668}\text{molm})^{-1}$
k_{sorb}	reaction coefficient	mol(sPa)^{-1}
K_{jk}	equilibrium constant of isotope exchange reaction	-

List of Symbols

L	length	m
m	mass	kg
N	molar amount	mol
n_{cyc}	number of cycles	-
p	pressure	Pa
R	ideal gas constant	$\text{J}(\text{molK})^{-1}$
T	temperature	K
t	time	s
u	velocity	$\text{m}(\text{s})^{-1}$
V	volume	m^3
x	position	m
z	molar fraction	-

Greek Symbols

α	separation factor	-
δ	smoothing factor hinge function	-
κ	adiabatic index	-
μ	viscosity	Pas
Ψ	stream ratio	-
ρ	density	$\text{kg}(\text{m}^3)^{-1}$
ξ	isotope dependent quantity	-

Subscripts

i	Isotopologue species Q ₂ : H ₂ , HD, HT, D ₂ , DT, T ₂
0	Reference state
abs	absorption
acc	accumulated
alpha	alpha phase
bleed	bleed stream
C1	Column 1 (Palladium)
C2	Column 2 (TiMn)
CC	closed cycle

col	column
cold	cold temperature
corr	correction
cyc	cycle
des	desorption
dos	dosed
eff	effective
end	columns end or bottom
eq	equilibrium
exch	exchange
exp	experiment
extr	extraction
f	fluid
feed	feed
feed-pipe	piping for feed supply
gas	gas phase related
head	columns head or top
heat	heating
heavy	heavy isotope species
hot	hot temperature
ic	intersect
id	ideal
in	inlet
inert	inert material
init	initialization
light	light isotope species
MAIA	set-up MAIA
mat	material
max	maximum
mid	middle
mix	mixture
mod	modified
OC	open cycle
oil	oil

List of Symbols

out	outlet
p	particle
PFR	plug flow reactor
port	sampling port
pre	pre-vessel
pseudo	pseudo-phase related
Q, j, k, l	atomic species Q: H, D, T
r	reaction
real	real
res	residual
RT	room temperature
set	set-point
sol	solid
sorb	absorption
SOS	speed of sound
source	source term
split	split ratio
SV	Sieverts
torus	torus throughput
tot	total

Superscripts

*	standard state
eq	equilibrium
G	gas phase
pseudo	pseudo-molecular transition phase
S	solid phase

Abbreviations

0D	Zero Dimensional
1D	One Dimensional
2D	Two Dimensional
BGA	Binary Gas Analyzer
C	Column
CANDU	Canadian Deuterium Uranium reactors
CC	Closed Cycle
CMH-TSA	Coupled Inverse and Normal Metal Hydride Reaction Temperature Swing Absorption
CSTR	Continuous Stirred Tank Reactor
DIRL	Direct Internal Loop
DIPAK	DIR Intergrated Development Platform Karlsruhe
EDX	Energy-dispersive X-ray Spectroscopy
EPS	Exhaust Processing System
EU-DEMO	European Demonstration Fusion Power Plant
GDS	Gas Distribution System
H	Hypothesis
HESTIA	Hydrogen Experiments for Separation with Temperature Initiated Absorption
HMI	Human Machine Interface

INTL	Inner Tritium Plant Loop
IRPR	Isotope Rebalancing & Protium Removal
ISS	Isotope Separation System
KIT	Karlsruhe Institute of Technology
MAIA	Material Investiagtion for Absorption
MFC	Mass Flow Controller
MS	Mass Spectrometer
OC	Open Cycle
OUTL	Outer Tritium Plant Loop
PEG	Plasma Enhancement Gases
PID	Piping and Instrumentation Diagram
PCI	Pressure-Concentration-Isotherm
PFR	Plug Flow Reactor/Reverser
PLC	Programmable Logic Controller
PSA	Pressure Swing Absorption
SEM	Scanning Electron Microscopy
SMB	Simulated Moving Bed
SNRL	Savannah River National Laboratories
TCAP	Temperature Cycling Absorption Process
TSA	Temperature Swing Absorption
V	Valve

Appendix A

Further Results of Material Development and Investigation

A.1 TiCr_x Alloys

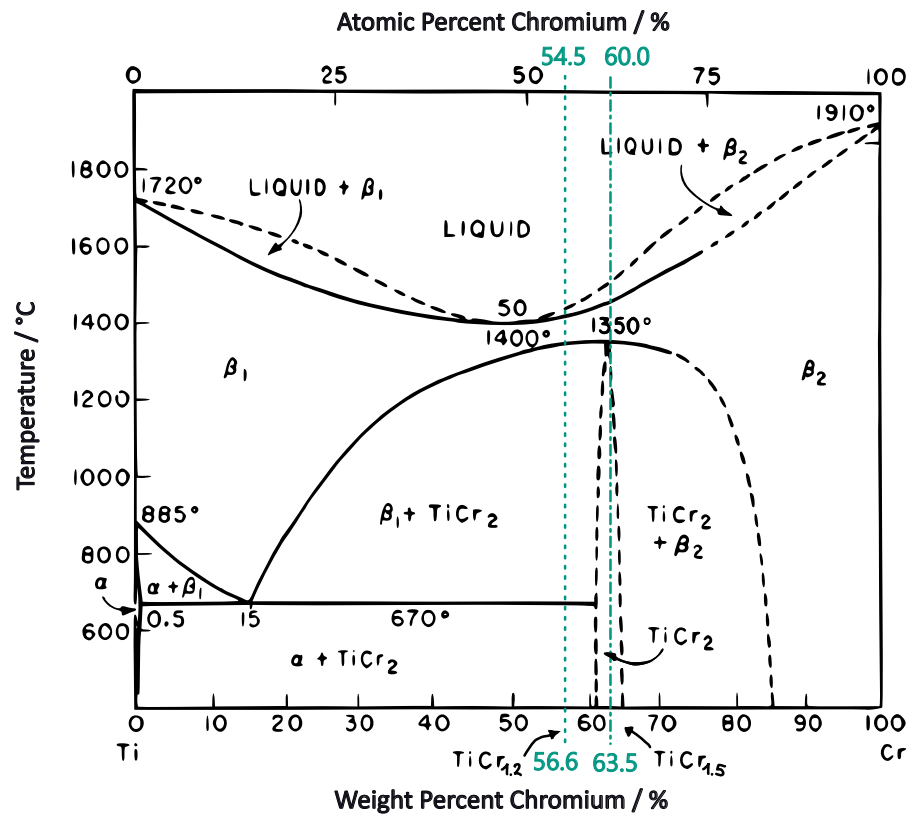


Figure A.1: Phase diagram of titanium and chromium adapted from [124]. Investigated $\text{TiCr}_{1.2}$ and $\text{TiCr}_{1.5}$ compositions are highlighted. Metastable β solid solutions transform to TiCr_2 and α -Ti by eutectic decomposition [125].

A.1. TiCr_x Alloys

Table A.1: SEM-EDX results of composition for TiCr_x cast alloys after heat treatment manufactured by IFAM.

Alloy	Ti-portion (target)		Cr-portion (target)	
	/at.%	/w.%	/at.%	/w.%
$\text{TiCr}_{1.2}$	49.9 ± 1.36 (45.4)	47.8 ± 1.36 (43.4)	50.1 ± 1.36 (54.5)	52.2 ± 1.36 (56.6)
$\text{TiCr}_{1.5}$	42.6 ± 0.8 (40)	40.6 ± 0.8 (36.5)	57.4 ± 0.8 (60)	59.4 ± 0.8 (63.5)

Table A.2: Phase proportions of TiCr_x alloys determined by Rietveld analysis.

Alloy	α -Titan /w.%	TiCr_2 /w.%
$\text{TiCr}_{1.2}$	$81.4 \% \pm 5 \%$	$18.6 \% \pm 5 \%$
$\text{TiCr}_{1.5}$	$90.5 \% \pm 5 \%$	$9.5 \% \pm 5 \%$

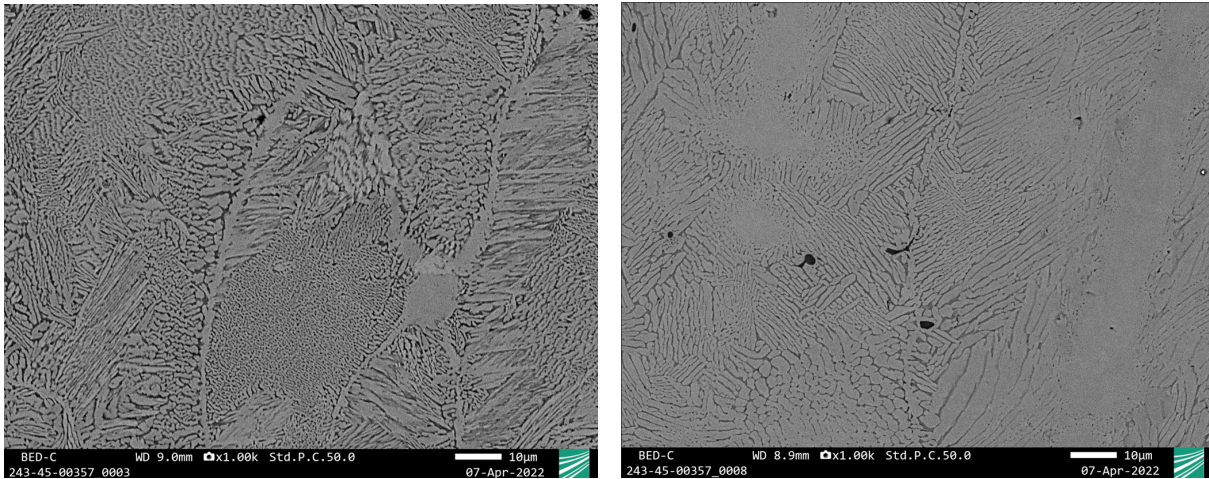


Figure A.2: Picture of $\text{TiCr}_{1.2}$ (left) $\text{TiCr}_{1.5}$ (right) phase constitution.

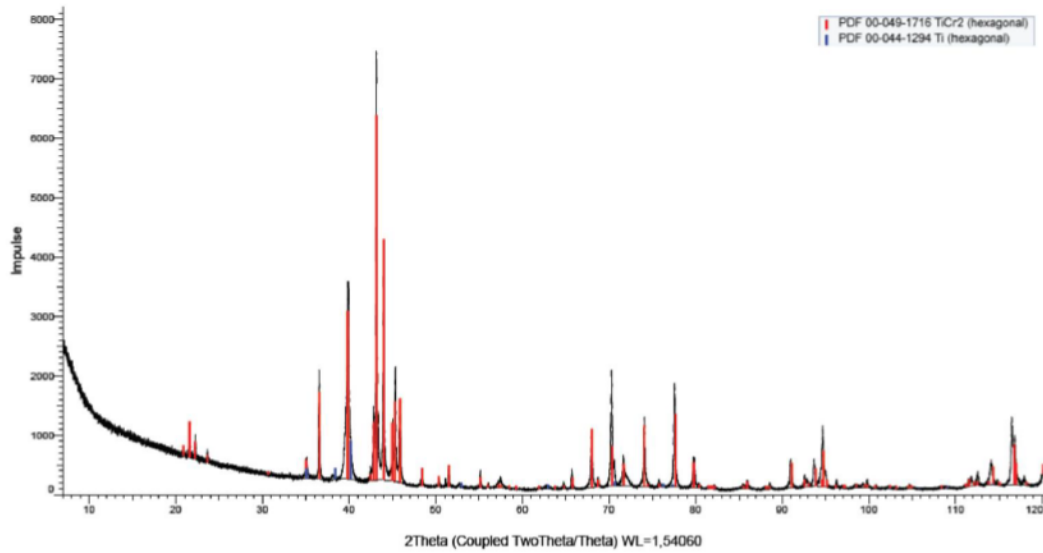


Figure A.3: Phase investigation of $\text{TiCr}_{1.2}$ using X-Ray analysis.

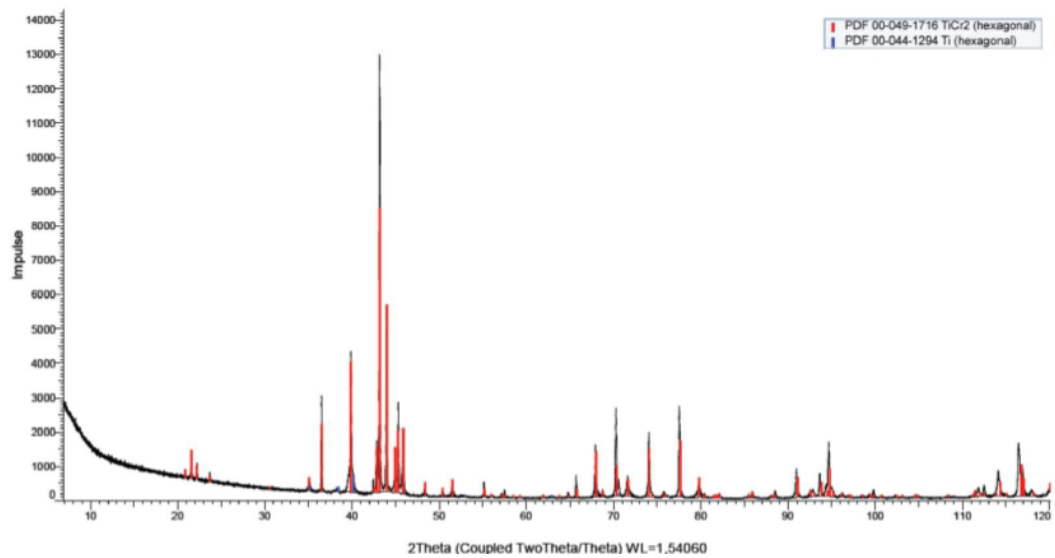


Figure A.4: Phase investigation of $\text{TiCr}_{1.5}$ using X-Ray analysis.

A.2 Multicomponent $\text{TiMn}_{1.5,\text{mod}}$ Alloys

Table A.3: SEM-EDX results of composition for $\text{TiMn}_{1.5}$ cast alloys after heat treatment manufactured by IFAM.

Element	Target value /at.%	Measured value /at.%
$\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.48}\text{Fe}_{0.10}\text{V}_{0.42}$ ($\text{TiMn}_{1.5,\text{mod}}$)		
Ti	29.76	32.25
Zr	4.75	4.94
Mn	46.86	45.45
Fe	3.17	3.81
V	13.3	13.54
$\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.38}\text{Fe}_{0.10}\text{V}_{0.52}$		
Ti	30.42	32.37
Zr	4.85	5.22
Mn	44.66	41.84
Fe	3.23	3.67
V	16.83	16.90

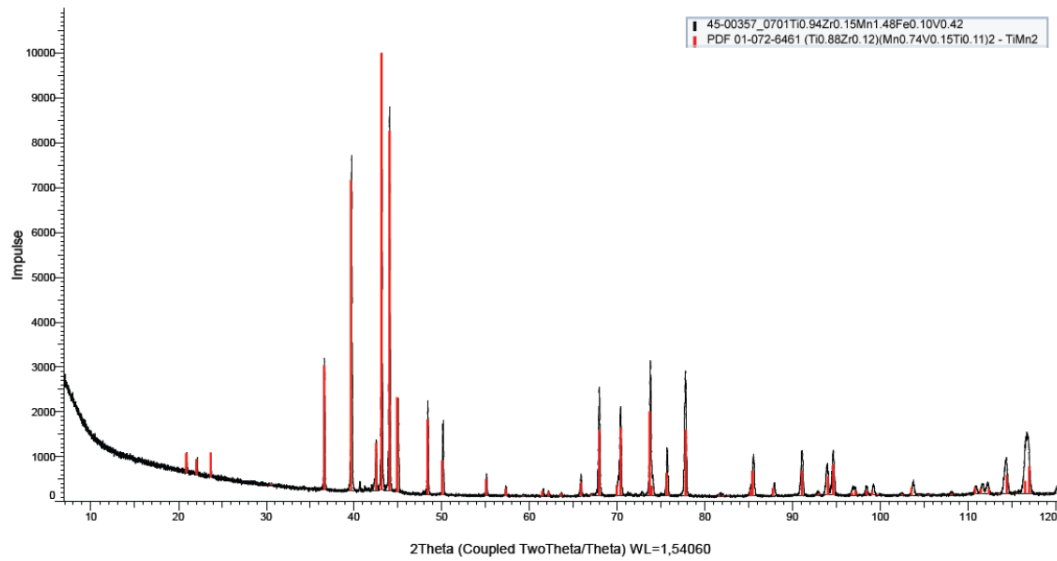


Figure A.5: Phase investigation of $\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.48}\text{Fe}_{0.10}\text{V}_{0.42}$ ($\text{TiMn}_{1.5,\text{mod}}$) using X-Ray analysis.

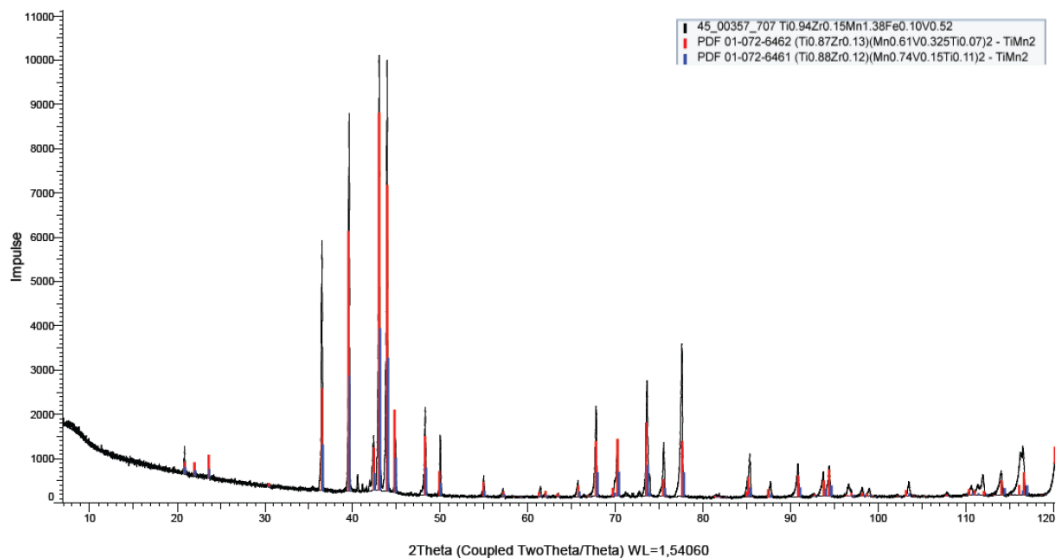


Figure A.6: Phase investigation of $\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.38}\text{Fe}_{0.10}\text{V}_{0.52}$ using X-Ray analysis.

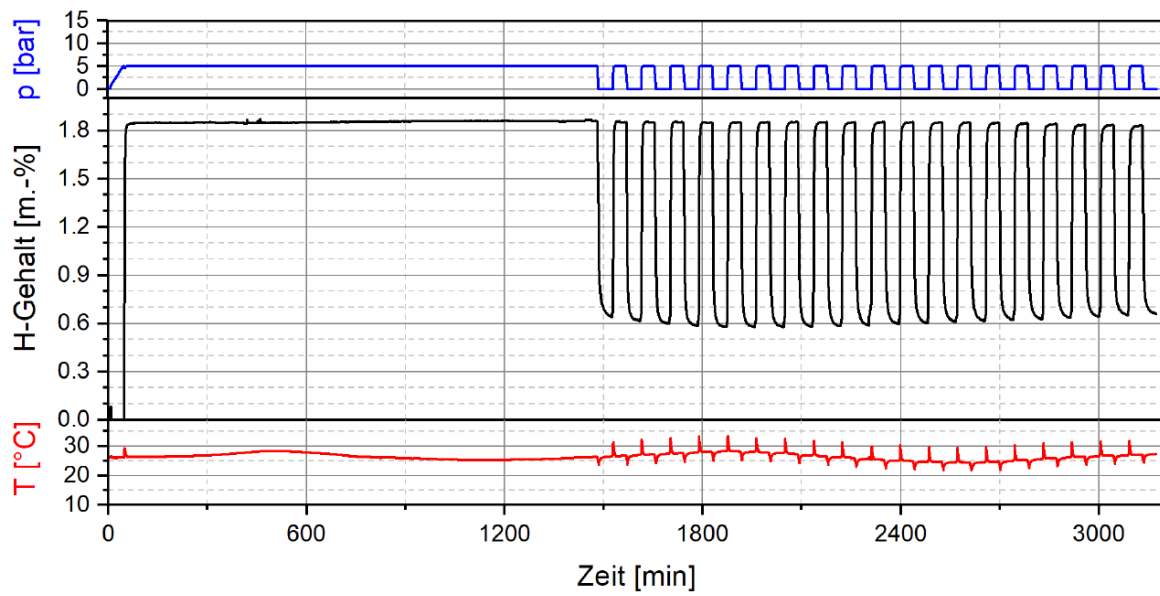


Figure A.7: Repeated hydrogen loading cycles of $\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.48}\text{Fe}_{0.10}\text{V}_{0.42}$ ($\text{TiMn}_{1.5,\text{mod}}$) using a magnet suspension balance.

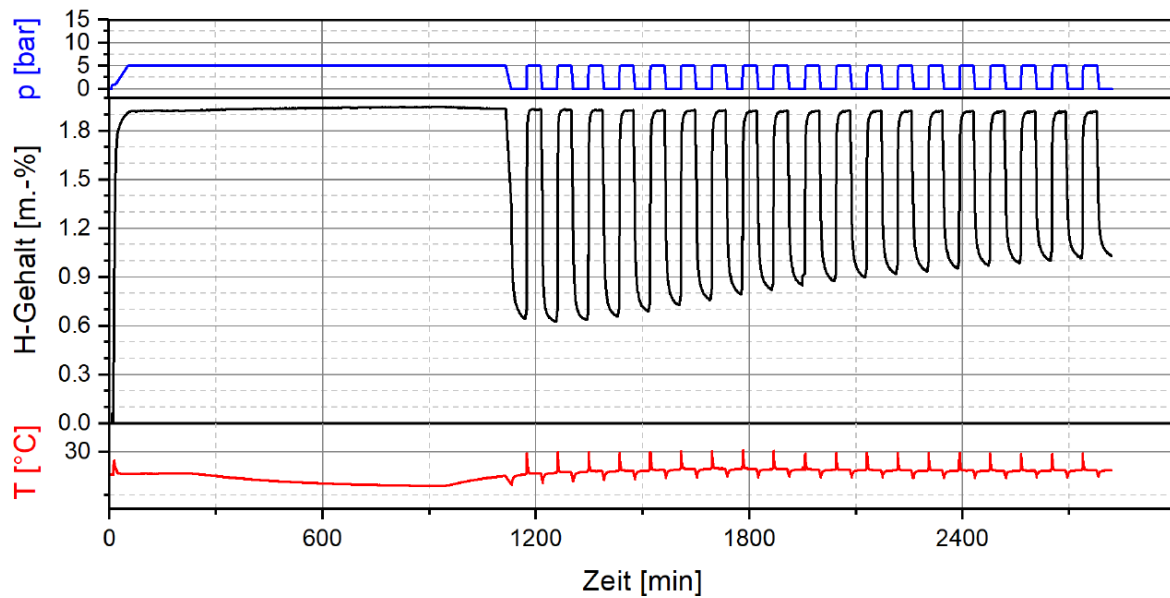


Figure A.8: Repeated hydrogen loading cycles of $\text{Ti}_{0.94}\text{Zr}_{0.15}\text{Mn}_{1.38}\text{Fe}_{0.10}\text{V}_{0.52}$ using a magnet suspension balance.

Appendix B

Further Information of Set-Ups

B.1 Experimental Set-Up MAIA

B.1.1 MAIA Sensor Uncertainties

A *Type B* uncertainty estimation is used to determine the error of the calculated concentrations c obtained by MAIA experiments according the *Guide to the expression of uncertainty measurement* [91].

Assuming the contributing uncertainties to be uncorrelated, the combined error $u(y)$ of the calculated quantity $y = f(x_1, x_2, \dots, x_N)$ is approximated by a first-order Taylor series according

$$u(y) = \sqrt{\sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i)} . \quad (\text{B.1})$$

In there, x_i equals a variable having an error $u(x_i)$, contributing to the determination of y . For the uncertainty of a MAIA experiment, y equals the concentration c of absorbed isotopes within the metal lattice follows from Eq. (3.2) and (3.4) and is required to determine a pressure-concentration-isotherm. The contributing independent uncertainties to be respected are those of the sample mass m_{mat} , the pressures p_{pre} and p_{MAIA} , the gas volumes V_{pre} and V_{MAIA} , the effective gas temperature $T_{\text{gas,MAIA}}$ and the uncertainty of the determined concentration c_{n-1} of the previous dosing step. Especially the latter adds up for increasing dosing steps n and causes the larger uncertainties for higher concentrations. The individual errors $u(x_i)$ follow from the manufacturer declaration for each utilized sensor given in Table B.1 or are obtained from the standard deviation of repeated volume calibration measurements described in Subsec. 3.1.1. For the determination of the sample mass and calibration volume a calibrated scale ($u(m) = 1 \cdot 10^{-5}$ g) was used.

B.2. Experimental Set-Up HESTIA

Table B.1: Utilized sensor uncertainties declared by manufacturer for determining PCIs from MAIA investigations. Uncertainties are used to calculate error bars of PCIs based on Type B uncertainty estimation [91].

Sensor ID	Sensor Name	Uncertainty	Reference
p_{pre}	10 bar Baratron <i>627F14MBC1B</i>	0.12 % of reading + 10^{-4} bar	[87]
$p_{\text{MAIA},1}$	10 bar Baratron <i>627F14MBC1B</i>	0.12 % of reading + 10^{-4} bar	[87]
$p_{\text{MAIA},2}$	1 bar Baratron <i>627F13MBC1B</i>	0.12 % of reading + 10^{-5} bar	[87]
T_{pre}	Thermocouple Type K	2.5 K	[126]
T_{MAIA}	Pt-100, class 1/3 B	$\frac{1}{3}$ (0.5 % of reading + 0.3 K)	[127]

B.2 Experimental Set-Up HESTIA

B.2.1 HESTIA Sensor Uncertainties

Table B.2: Utilized sensor uncertainties declared by manufacturer for sensors used to obtain experimental values of HESTIA experiments.

Sensor ID	Sensor Name	Uncertainty	Reference
p1	1 bar Baratron <i>627F13MBC1B</i>	0.12 % of reading + 10^{-5} bar	[87]
p2	10 bar Baratron <i>627F14MBC1B</i>	0.12 % of reading + 10^{-4} bar	[87]
p3	1 bar Baratron <i>627F13MBC1B</i>	0.12 % of reading + 10^{-5} bar	[87]
p4	10 bar Baratron <i>627F14MBC1B</i>	0.12 % of reading + 10^{-4} bar	[87]
T1	Pt-100, class 1/3 B	$\frac{1}{3}$ (0.5 % of reading + 0.3 K)	[127]
T2	Pt-100, class 1/3 B	$\frac{1}{3}$ (0.5 % of reading + 0.3 K)	[127]
T3	Pt-100, class 1/3 B	$\frac{1}{3}$ (0.5 % of reading + 0.3 K)	[127]
T4	Pt-100, class 1/3 B	$\frac{1}{3}$ (0.5 % of reading + 0.3 K)	[127]
BGA	BGA244	Resolution: 0.001 m/s; Accuracy: ± 0.05 %	[98]

B.2.2 Mass Spectrometer

Mass spectrometers are common analytical devices due to their capability of distinguishing between isotopes and fragments of large molecules. The measurement principle is based on ionizing a gas sample and accelerating the resulting charged ion fragments into a (quadrupole) magnet field. Due to the different masses and charges of the ion fragments, a mass/charge (m/z) specific ion current spectrum is measured, which can be correlated to elements and functional group species. For distinguishing hydrogen isotopes, especially the abundance of the $m/z = 1$ (H), 2 (H_2 ,D), 3 (HD) and 4 (D_2) are of interest and require the utilization of a *High resolution MS*. Thereby the double occupancy of m/z 2 and the typically low abundance of H^+ ion fractions is challenging.

In addition, MSs are known for being very sensitive and prone towards impurities even in ppm range (qualitative). Furthermore, only very small sample amounts are necessary for the measurement principle, demanding for reduced sample pressures of at least $5 \cdot 10^{-4}$ mbar (maximum operation pressure tolerated by faraday cup [128]). Here the challenge is to enable this reduction without influencing the sample composition. This is critical especially for isotopes, as the different masses affect their specific pumping speeds. Thus utilization of vacuum pumping systems may cause isotope effects and lead to misinterpretation of the TSA process efficiency. [129]

B.3 P&IDs of Set-Ups

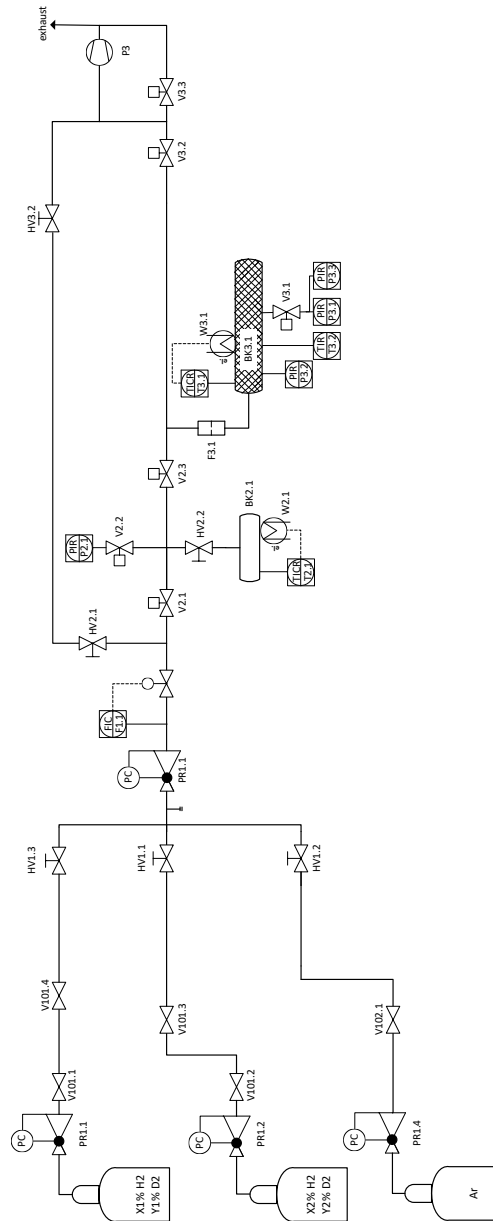


Figure B.1: P&ID of custom set-up MAIA.

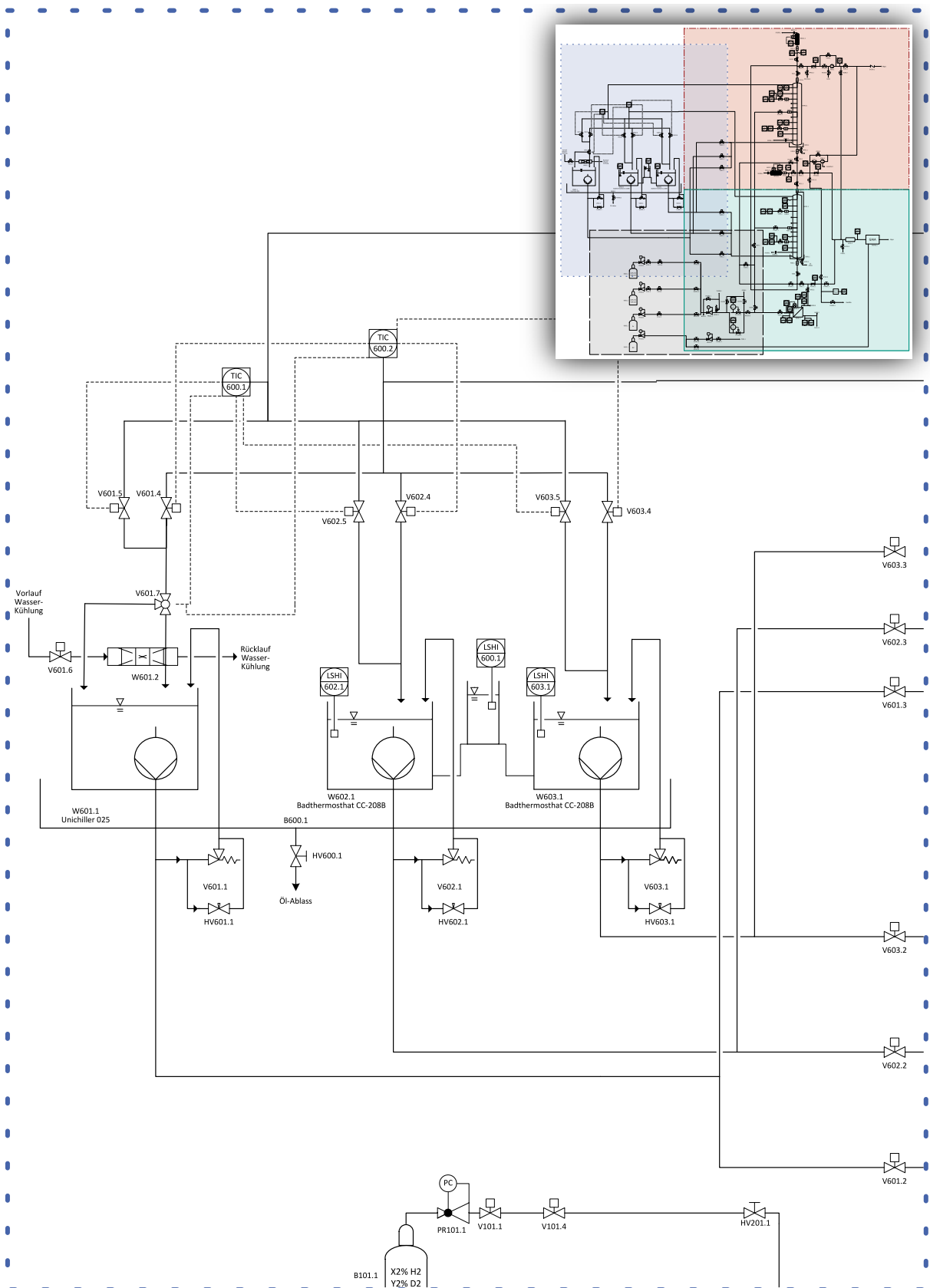


Figure B.2: P&ID section of heating and cooling system of laboratory set-up HESTIA.

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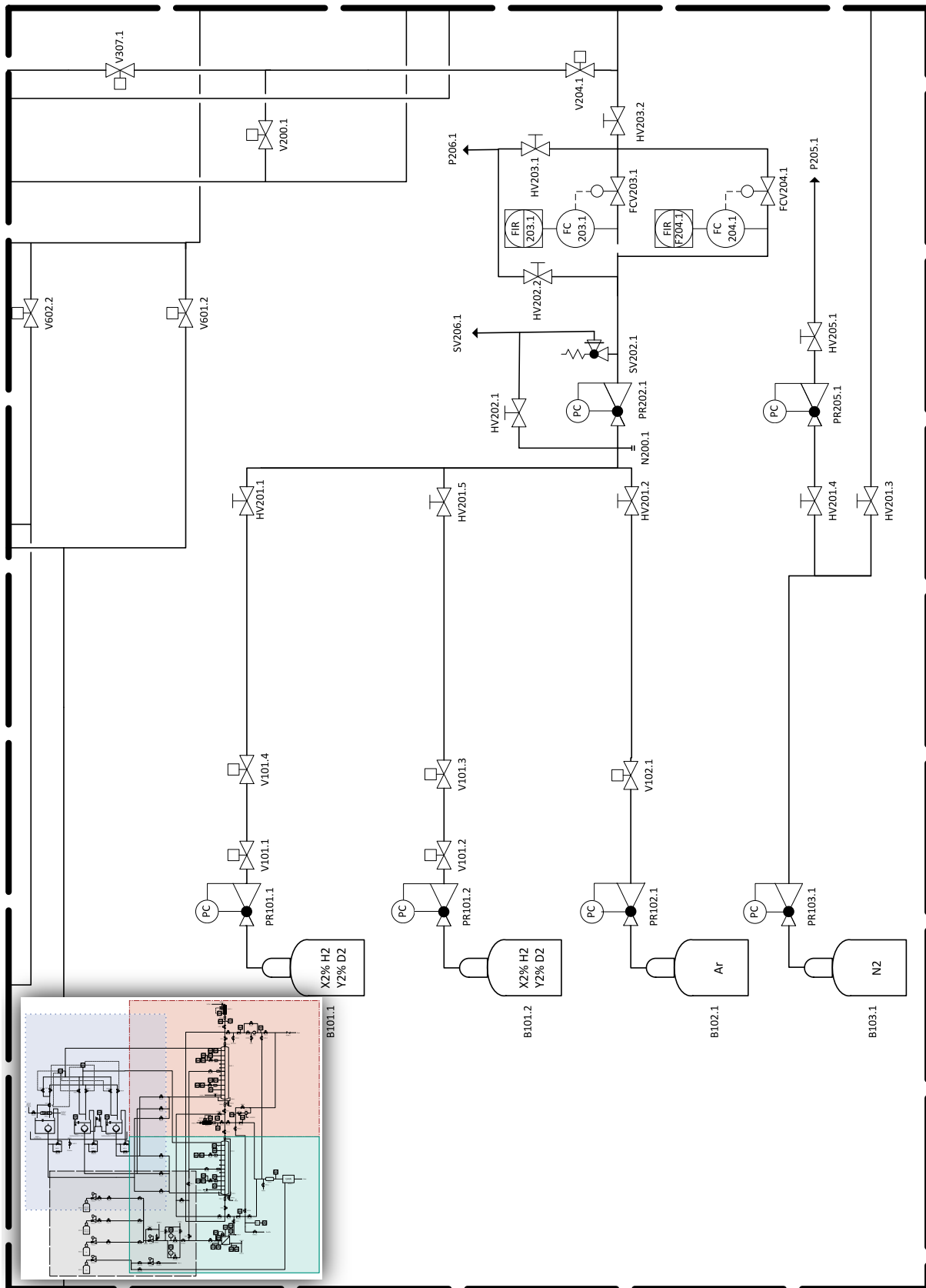


Figure B.5: P&ID section of gas supply section of laboratory set-up HESTIA.

Appendix C

Further Results of Simulations

C.1 Simulations to Mimic HESTIA Operation

Table C.1: Overview of utilized geometry, process step and material parameters to mimic HESTIA experiments.

Parameter	Value	Unit
Geometry		
Length	1.05	m
Diameter	0.006	m
Particle diameter	$8 \cdot 10^{-4}$	m
material amount	Pd: 0.8584, TiMn: 0.0881	mol
nodes per column	20	-
Process step times		
t_{exch}	120	s
t_{heat}	600	s
t_{extr}	10	s
Further Parameters		
k_{heat}	50	Wm/K
k_{p}	$3.5 \cdot 10^7$	sPa ² /K ^{1.668}
ΔH_{sorb}	Pd: -31925, TiMn: -35665	J/mol
k_{sorb}	$5 \cdot 10^{-6}$	mol/sPa
c_{p}^{S}	500	J/kgK
ρ^{S}	7870	kg/m ³
hys	Desorption: Pd: 0.71, TiMn: 0.83	-
	Absorption: Pd: 1, TiMn: 1	-

C.1. Simulations to Mimic HESTIA Operation

Table C.2: Overview of utilized initialization parameters and process temperatures to mimic HESTIA operation. Schematic description of investigated process operation variants are given in Figure 4.6 and 4.8. Continuation of Table C.1.

Single separation efficiency experiments (Fig. 4.6)			
Parameter	Variant 1	Variant 2	Unit
$c_{\text{init,Pd}}$	0.63	/	$\text{mol}_Q/\text{mol}_{\text{mat}}$
$c_{\text{init,TiMn}}$	/	0.55	$\text{mol}_Q/\text{mol}_{\text{mat}}$
$p_{\text{init,Pd}}$	280	/	mbar
$p_{\text{init,TiMn}}$	/	290	mbar
$p_{\text{init,PFR}}$	260	265	mbar
$T_{\text{init,Pd}}$	293.15	/	K
$T_{\text{init,TiMn}}$	/	263.65	K
$T_{\text{init,PFR}}$	293.15	293.15	K
$N_{Q2,\text{tot}}$	0.054	0.051	mol
$\dot{N}_{\text{extr,Pd}}$	$4 \cdot 10^{-4}$	/	mol/s
$\dot{N}_{\text{extr,TiMn}}$	/	$1.8 \cdot 10^{-4}$	mol/s
$T_{\text{hot,Pd}}$	415.15	/	K
$T_{\text{cold,Pd}}$	293.15	/	K
$T_{\text{hot,TiMn}}$	/	329.65	K
$T_{\text{cold,TiMn}}$	/	263.65	K
$T_{\text{hot,PFR}}$	293.15	293.15	K
$T_{\text{cold,PFR}}$	293.15	293.15	K
Separation experiments with both columns (Fig. 4.8)			
Parameter	Variant 4	Variant 5	Unit
$c_{\text{init,Pd}}$	0.7	0.7	$\text{mol}_Q/\text{mol}_{\text{mat}}$
$c_{\text{init,TiMn}}$	0.25	0.25	$\text{mol}_Q/\text{mol}_{\text{mat}}$
$p_{\text{init,Pd}}$	840	840	mbar
$p_{\text{init,TiMn}}$	830	830	mbar
$T_{\text{init,Pd}}$	293.15	293.15	K
$T_{\text{init,TiMn}}$	333.15	333.15	K
$N_{Q2,\text{tot}}$	0.054	0.054	mol
$\dot{N}_{\text{extr,Pd}}$	$4.51 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	mol/s
$\dot{N}_{\text{extr,TiMn}}$	$3.38 \cdot 10^{-4}$	$2.99 \cdot 10^{-4}$	mol/s
$T_{\text{hot,Pd}}$	421.15	422.65	K
$T_{\text{cold,Pd}}$	293.15	293.65	K
$T_{\text{hot,TiMn}}$	333.65	333.65	K
$T_{\text{cold,TiMn}}$	268.15	268.65	K
Initialization			
$z_{j,\text{init}}^S$	$z_{\text{H,init}}^S = z_{\text{D,init}}^S = 0.5$		-
$z_{i,\text{init}}^G$	$z_{\text{HD,init}}^G = 1$		-

Table C.3: Overview of initialization parameters and process temperatures for simulations comparing the impact on the extracted product composition by utilizing a TiMn column instead of an inert PFR using HESTIA geometries for demonstration case. Geometry, process step and material parameters are given in Table C.1.

Single separation efficiency Pd Column - Variant 1		
Parameter	Value	Unit
$c_{\text{init,Pd}}$	0.62	$\text{mol}_Q/\text{mol}_{\text{mat}}$
$p_{\text{init,Pd}}$	270	mbar
$p_{\text{init,PFR}}$	255	mbar
$T_{\text{init,Pd}}$	293.15	K
$T_{\text{init,PFR}}$	293.15	K
$N_{Q_2,\text{tot}}$	0.053	mol
$\dot{N}_{\text{extr,Pd}}$	$4.24 \cdot 10^{-4}$	mol/s
$T_{\text{hot,Pd}}$	423.15	K
$T_{\text{cold,Pd}}$	293.15	K
$T_{\text{hot,PFR}}$	293.15	K
$T_{\text{cold,PFR}}$	293.15	K
Separation efficiency of both Columns - Variant 4		
Parameter	Value	Unit
$c_{\text{init,Pd}}$	0.7	$\text{mol}_Q/\text{mol}_{\text{mat}}$
$c_{\text{init,TiMn}}$	0.245	$\text{mol}_Q/\text{mol}_{\text{mat}}$
$p_{\text{init,Pd}}$	800	mbar
$p_{\text{init,TiMn}}$	810	mbar
$T_{\text{init,Pd}}$	293.15	K
$T_{\text{init,TiMn}}$	333.15	K
$N_{Q_2,\text{tot}}$	0.053	mol
$\dot{N}_{\text{extr,Pd}}$	$4.24 \cdot 10^{-4}$	mol/s
$\dot{N}_{\text{extr,TiMn}}$	$4.24 \cdot 10^{-4}$	mol/s
$T_{\text{hot,Pd}}$	423.15	K
$T_{\text{cold,Pd}}$	293.15	K
$T_{\text{hot,TiMn}}$	333.15	K
$T_{\text{cold,TiMn}}$	263.15	K
Initialization		
$z_{j,\text{init}}^S$	$z_{\text{H},\text{init}}^S = z_{\text{D},\text{init}}^S = 0.5$	-
$z_{i,\text{init}}^G$	$z_{\text{HD},\text{init}}^G = 1$	-

C.1. Simulations to Mimic HESTIA Operation

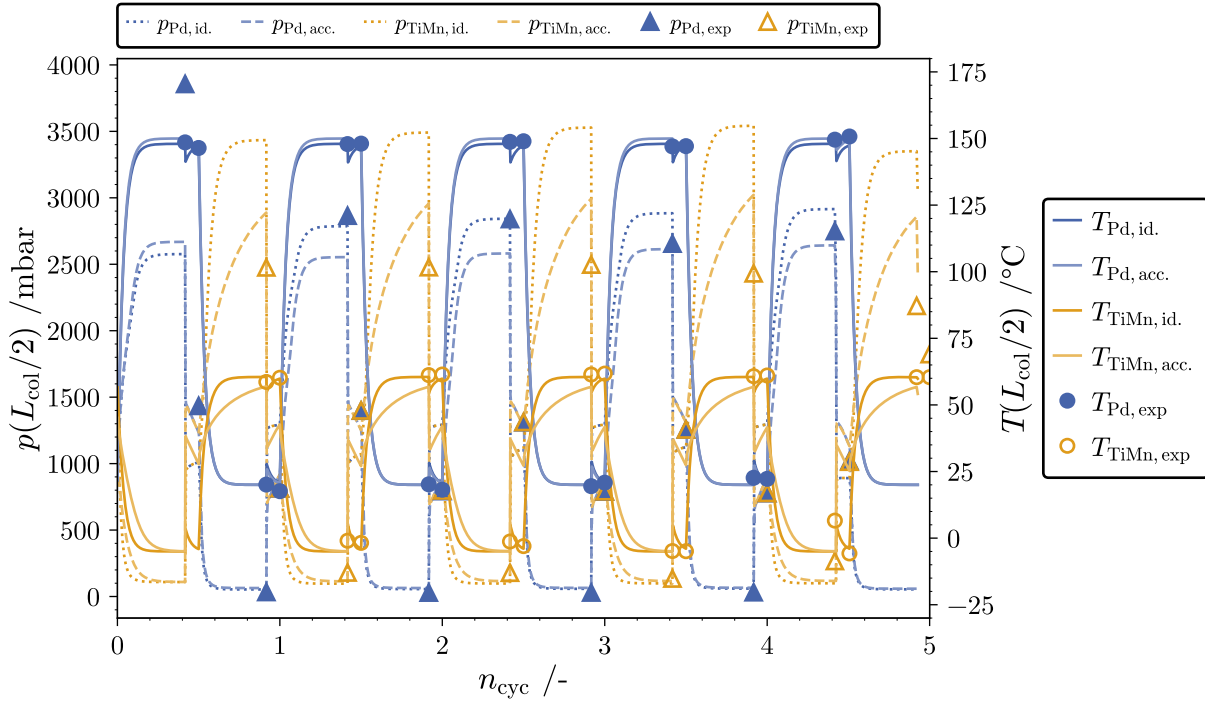


Figure C.1: Simulated pressure and temperature profiles of the normal operation HESTIA experiment compared to experimental values. TiMn characteristics are respected by ideal behavior (id.) in comparison to accumulation (acc.) within the column. Error bars are smaller than the symbols.

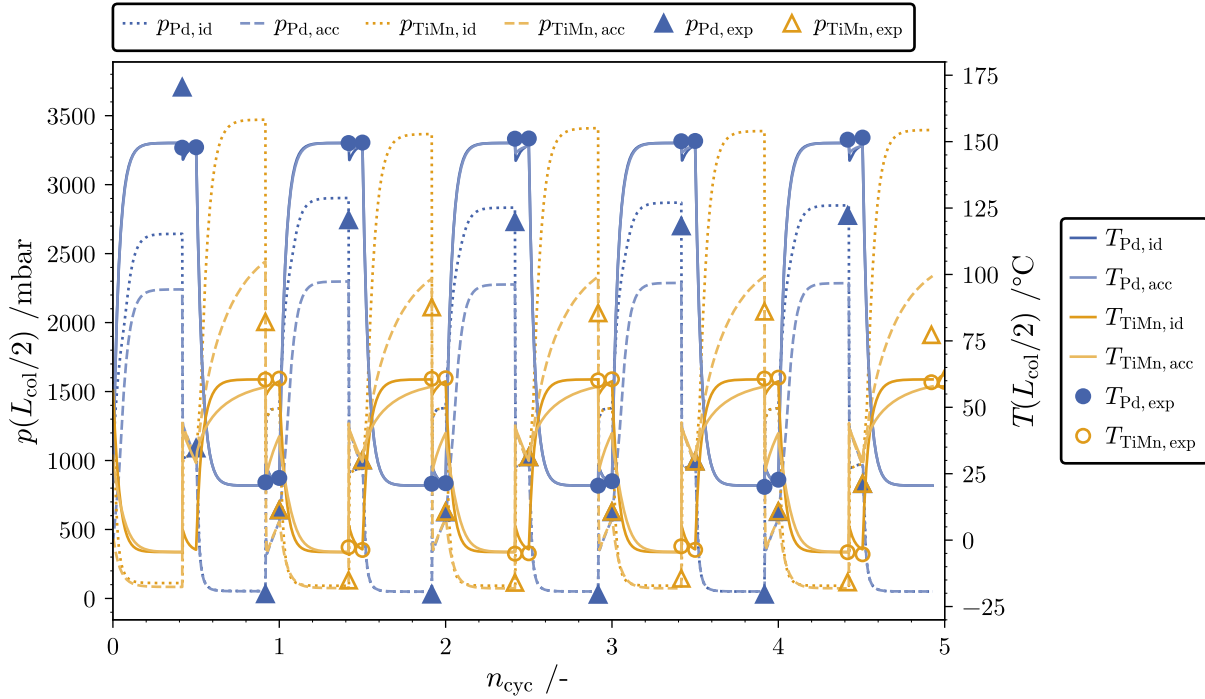


Figure C.2: Simulated pressure and temperature profiles of the exchange variant HESTIA experiment compared to experimental values. TiMn characteristics are respected by ideal behavior (id.) in comparison to accumulation (acc.) within the column. Error bars are smaller than the symbols.

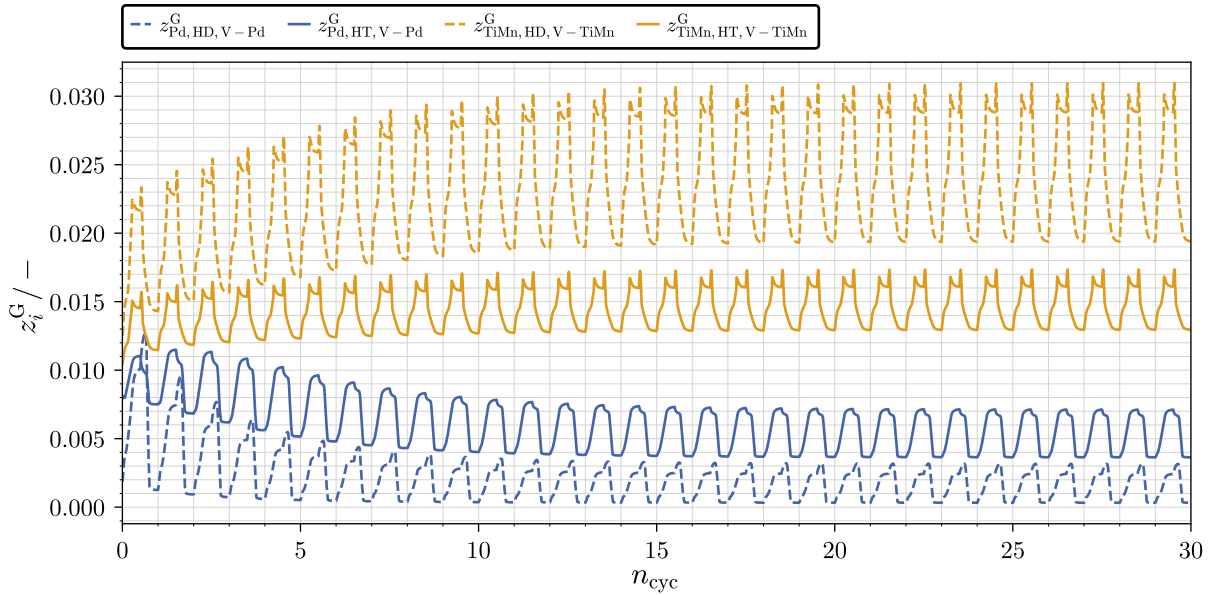
C.2 EU-DEMO IRPR Simulations

Table C.4: Utilized parameters for IRPR operation simulation.

Parameter	Value	Unit
Geometry		
Length	10	m
Diameter	0.01	m
Particle diameter	0.001	m
material amount	4	mol
Q ₂ amount	1.82	mol
nodes per column	20	-
Process step times		
t_{exch}	200	s
t_{heat}	400	s
$t_{\text{extr,Pd}}$	$(1 - \Psi_{\text{split}}) \cdot t_{\text{feed}}$	s
$t_{\text{extr,TiMn}}$	$\Psi_{\text{split}} \cdot t_{\text{feed}}$	s
t_{feed}	180	s
Feed composition and flow rates		
$\dot{N}_{\text{feed}} = \dot{N}_{\text{extr}}$	0.001	mol/s
$z_{\text{feed},i}^{\text{G}}$	$z_{\text{feed,H}_2}^{\text{G}} = 0.01,$ $z_{\text{feed,D}_2}^{\text{G}} = z_{\text{feed,T}_2}^{\text{G}} = 0.245,$ $z_{\text{feed,D}_T}^{\text{G}} = 0.49$	-
Ψ_{split}	0.15	-
Process temperatures and further Parameters		
T_{hot}	Pd: 393.15, TiMn: 333.15	K
T_{cold}	Pd = TiMn: 273.15	K
k_{heat}	50	Wm/K
k_{p}	$3.5e^7$	sPa ² /K ^{1.668}
ΔH_{sorb}	Pd: -31925, TiMn:-35665	J/mol
k_{sorb}	$5e^{-6}$	mol/sPa
c_{p}^{S}	500	J/kgK
ρ^{S}	7870	kg/m ³
hys	Desorption: Pd: 0.71, TiMn: 0.83	-
	Absorption: Pd: 1, TiMn: 1	-

Table C.5: Continuation of utilized parameters and initialization for IRPR operation simulation.

Parameter	Value	Unit
Initialization		
Pd Column		
c	0.65	$\text{mol}_Q/\text{mol}_{\text{mat}}$
p	1400	mbar
T	273.15	K
$z_{j,\text{init}}^S$	$z_{T,\text{init}}^S = z_{D,\text{init}}^S = 0.495,$ $z_{H,\text{init}}^S = 0.01$	-
$z_{i,\text{init}}^G$	$z_{DT,\text{init}}^G = 1$	-
$N_{Q2,\text{tot}}$	1.31	mol
TiMn Column		
c	0.25	$\text{mol}_Q/\text{mol}_{\text{mat}}$
p	1400	mbar
T	333.15	K
$z_{j,\text{init}}^S$	$z_{T,\text{init}}^S = z_{D,\text{init}}^S = 0.495, z_{H,\text{init}}^S = 0.01$	-
$z_{i,\text{init}}^G$	$z_{DT,\text{init}}^G = 1$	-
$N_{Q2,\text{tot}}$	0.508	mol


Figure C.3: Establishing composition of hetero-isotopologues HD and HT in the gas phase at the extraction port of the Pd and TiMn column in dependence of the number of performed cycles in total reflux mode. Compositions run into steady state after ~ 10 closed cycles.

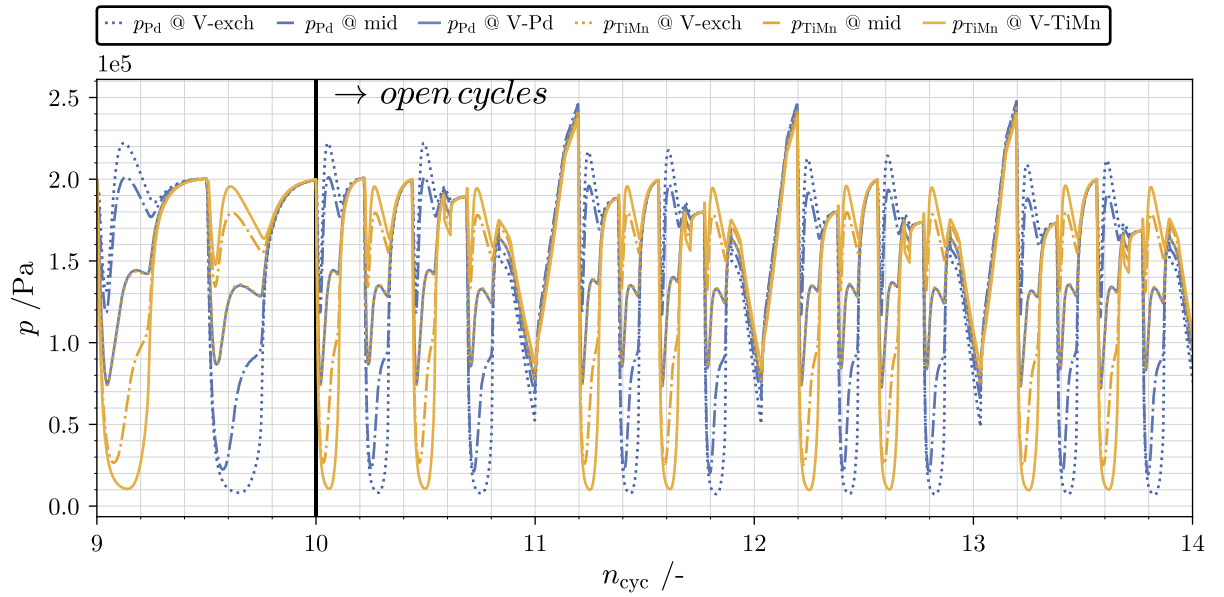


Figure C.4: Simulated pressure profiles for the palladium and the TiMn column in dependence of the performed process cycles. After 10 cycles in total reflux mode, open cycles are tolerated, extracting 15 % of the total column inventory during sampling in absorption phase (cold extraction). At $n_{CC} = 11, 12$ and 13 pressure increases caused by feeding are observable, while the pressure decreases as consequence of the product withdrawal are visible at $n_{CC} \approx 10.9, 11.9$ and 12.9 (Pd) and $n_{CC} \approx 10.7, 11.7$ and 12.7 (TiMn).

