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By-Product Hydrogen to Fuel Cell Vehicles

A Summary of Available Purification Methods for Surplus Hydrogen Gas from Sodium Chlorate Production, and Status of Hydrogen Purity Analyses

Degree Project in Chemistry and Chemical Engineering

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Abstract

With the prompt establishment of fuel cell vehicles, industries with large hydrogen assets are becoming interested to join the building of a hydrogen infrastructure. AkzoNobel owns several sodium chlorate facilities that are generating hydrogen as a by-product. This hydrogen is not pure enough for fuel cell applications and the purpose of this project has been to identify potential purification methods and how the analytical part works in practice. This has been executed by literature reviews and E-mail conversations with relevant people.

The results show that pressure swing adsorption (PSA) and palladium membrane diffusion are purification methods that currently are able to purify hydrogen to fuel cell quality. The PSA system is suitable to use when it comes to purifying the whole hydrogen capacity (3800 Nm³/h H₂ from a 50 kton/y plant) with a recovery of 70% to 2660 Nm³/h of 5N graded hydrogen. Palladium membrane diffusion is a better alternative for smaller applications. The company SAES Pure Gas provides palladium purifiers with capacities up to 140 Nm³/h. One of these can be used to purify a part of the hydrogen stream to 9N graded quality with just 2% bleed.

Analyzing the impurities listed in the ISO 14687-2 standard is difficult and expensive, and it is just a few laboratories that can complete the whole standard. The Swedish institute SP has developed their own analysis methods and is currently able to analyze 9 of 14 impurities. When the rest of the impurities can be analyzed, SP will offer hydrogen sampling and analyses to industries.

Further work needs to be applied in form of laboratory trials to ensure that all impurities are below the maximum concentrations for the desired purification method. The analysis methods in general need to be further improved and/or the ISO 14687-2 standard needs to be reformed to allow more hydrogen producers to join the infrastructure.

Keywords: Sodium Chlorate, By-product hydrogen, Hydrogen purification, Pressure swing adsorption (PSA), Palladium membrane diffusion, Fuel cell vehicles (FCVs), ISO 14687-2

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1. Introduction

Since the beginning of the industrial era in the 18th century, carbon dioxide (CO₂) emissions to the atmosphere have risen heavily and resulted in that the current concentration of CO₂ is 30% higher than usual. The increased amount of greenhouse gases and their accumulations in the atmosphere have been predicted to cause several environmental effects. The global political scene has acted and formulated protocols and other agreements that together attempts to reduce the CO₂ emissions worldwide. [1]

The transportation sector alone is responsible for about 25% of the CO₂ emissions worldwide. Three quarters of the sector is represented by road associated vehicles such as cars and trucks that almost entirely rely on fossil fuels. In the future it is expected that the worldwide vehicle ownership will increase further, which results in additional CO₂ emissions. [2] This is the reason of the high demand of finding alternative fuels to vehicles or optimizing the existing internal combustion engines to be more effective and more environmental friendly. Zero emission vehicles, typically electric and fuel cell powered vehicles, have been through a remarkable development and increases in popularity. Fuel cell vehicles that uses hydrogen as fuel, is one of the building blocks of the hydrogen economy that can potentially replace oil in the future. [3]

Hydrogen is the simplest element, where the main isotope consists of one proton and one electron. It is the most abundant element in the universe and essentially the source of all energy, according to the fusion reaction to helium in stars. On the other hand, hydrogen gas does not naturally exist in the earth's atmosphere, which means that hydrogen just occurs as a part of other molecules like water and organic substances. This means that to be able to use hydrogen as a fuel, the hydrogen gas must be extracted and isolated from various sources e.g. fossil fuels, biomass or water. The production method will determine the environmental aspects of hydrogen, just like for the electricity production to electric vehicles. [4, 5]

One of the biggest challenges when it comes to fuel cell vehicles is to extend a fueling infrastructure when the number of cars is low. In the early state, the hydrogen contribution will mostly rely on fossil fuels. In the future, by-product hydrogen from industries (e.g. sodium chlorate) may be used and water electrolysis becomes more economical feasible. [6]

1.1 Purpose and Objectives

The purpose of this degree project is to investigate the availability of hydrogen purification and analysis methods, for AkzoNobel sodium chlorate facilities, that could achieve hydrogen pure enough for fuel cell applications. The objectives that have been attended:

- Summarize available purification methods for hydrogen gas, their characteristic area of application (what they remove and how pure the gas gets) and other pros and cons.
- Propose a combination of purification methods that would result in a gas pure enough to be used in car fuel cells.
- Identify suitable analysis methods for the impurities present in the hydrogen gas from the chlorate production
- Identify companies and institutes that can perform sampling and analysis of the impurities in the hydrogen gas in a proper way at the low concentrations present

1.2 Delimitations

This is a literature review where no laboratory attempts have been applied due to that it is just the first step in the development. No optimization, neither technical nor economical, was included. The focus is the Swedish market.

1.3 Methods

The study was performed by four major approaches;

1. Understanding the hydrogen situation around AkzoNobel sodium chlorate facilities by contacting employees in charge via E-mail and phone calls.
2. Identifying companies or institutes that could share/offer useful information or future services.
3. Literature reviews by using Chalmers library academic search engine *Summon* to find E-books and articles.
4. Internet search.

2. Background

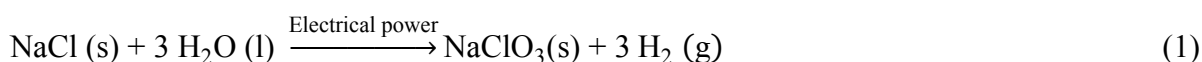
This chapter brings some information that is good to know for understanding the results and to conceive the approach to examining the problem.

2.1 Sodium Chlorate

Sodium chlorate (NaClO_3) is a white crystalline compound with strong oxidizing potential and function as an oxidizing agent. The main application of sodium chlorate is in the pulp and paper industry when manufacturing the bleaching agent chlorine dioxide (ClO_2). This chemical is the main component in so called elemental-chlorine free (ECF) bleaching of chemical pulp. The current world production of sodium chlorate is approximately 3 million metric tons annually and AkzoNobel, with its 14 production sites, is the largest producer with a total amount of about 1 million metric ton sodium chlorate each year. [7]

2.1.1 Process Description

Continuous production of sodium chlorate general consist of three main sections; brine treatment, electrolysis and crystallization. This is an electrochemical process that uses high quality sodium chloride and water as raw materials together with a substantial amount of electricity to power the electrolysis cells. The final product is obtained either as crystals or in aqueous solution depending on customer requirements. Hydrogen gas is produced as a by-product in the electrolysis cells, and will be further described in section 2.1.2. The overall reaction of the chlorate process is presented in Equation 1. A more detailed description of the process is found in Appendix A. [8]



2.1.2 By-Product Hydrogen

As noticed in the previous section, hydrogen gas is a by-product with a 3 to 1 molar ratio compared to sodium chlorate, described in Equation 1. Roughly 60 kg hydrogen is formed per ton sodium chlorate. This hydrogen can, for example, be used internally as burner gas (e.g. to power the chlorate dryer) or be sold to customers for hydrogenation purposes. If the hydrogen gas does not suit any function, it is ventilated to the atmosphere. The hydrogen gas, however, must undergo a purification procedure before any action. [9]

The main impurity that needs to be reduced is chlorine. Small amounts of chlorine will always escape from the electrolysis cells and merge with the hydrogen gas. The chlorine must be removed because it could cause problems with corrosion, health, odor and environment. This is typically done by absorbing it in alkaline solution in packed bed scrubbers. [10]

Oxygen formation occurs from side reactions during the electrolysis and needs to be controlled or reduced for safety reasons. If the hydrogen is supposed to be used for hydrogenation purposes, it is common to let the oxygen react with hydrogen to form water (Equation 2) in a deoxo reactor. In this reactor it is also important to control the water-gas shift equilibrium between carbon dioxide and monoxide to ensure that only small amounts of carbon monoxide are formed, see Equation 3. [10]



Figure 1 shows a typical hydrogen purification system with different scrubbers, a carbon filter to complete the removal of chlorine and a deoxo reactor. [10]

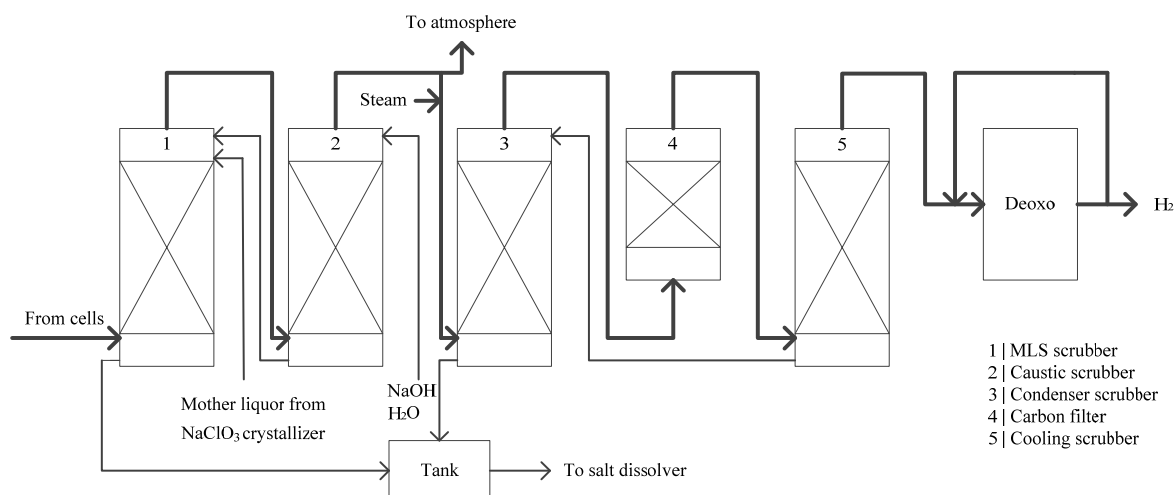


Figure 1: Overview of a typical sodium chlorate hydrogen purification system.

Information about the purity of the hydrogen gas is important when considering new usage of the hydrogen. Typical levels of various impurities are given in Table 1. The data indicate that the hydrogen is not pure enough according to the standard (see Appendix B), more about that in section 2.2.3. [10]

| Impurity | Chemical formula | Amount | Unit |
|------------------|------------------|--------|---------|
| Oxygen | O ₂ | <10 | mol-ppm |
| Water | H ₂ O | <50 | mol-ppm |
| Methane | CH ₄ | <100 | mol-ppm |
| Nitrogen | N ₂ | <2000 | mol-ppm |
| Carbon monoxide | CO | <1 | mol-ppm |
| Hydrogen sulfide | H ₂ S | <1 | mol-ppm |
| Chlorine | Cl ₂ | <1 | mol-ppm |
| Carbon dioxide | CO ₂ | <200 | mol-ppm |
| Hydrogen index | H ₂ | >99.7 | mol% |

Table 1: Typical concentrations of various impurities in the hydrogen gas after purification.

2.2 Usage of Hydrogen for Fuel Cell Applications

The basic principle of fuel cells was discovered in 1839 by William Grove during an experiment when he was trying to reverse the electrolysis of water. Grove discovered that his invention was an electrochemical device that could accomplish a continuous conversion from chemical to electric energy as long as the device was supplied with fuel and an oxidant. In 1960 the researchers began to build fuel cells for practical applications, which has been a big research area ever since. [11]

2.2.1 Proton Exchange Membrane Fuel Cell

The most common type of fuel cell for commercial applications is the proton exchange membrane fuel cell (PEMFC). The principle of a PEMFC is that inlet hydrogen splits into protons and electrons on a platinum surface at the anode (Equation 4). The protons will diffuse through a solid polymer electrolyte, while the electrons transfer through an outside circuit to the cathode side. At the cathode, oxygen reacts with the migrated protons and the by-passed electrons, which yields water as product according to Equation 5. These half-reactions will give the overall electrochemical reaction in Equation 6. The energy is utilized as electrical work in the external circuit. [12]



Theoretically, a PEMFC could give about 1 V, but practically a lower voltage is obtained. To generate higher voltages, multiple PEMFCs must be connected in series. The maximum theoretical efficiency of a PEMFC is 83%. This is determined from the ratio between the Gibbs free energy and the enthalpy (hydrogen higher heating value) at 25 °C, see Equation 7. In reality, it is more likely to achieve efficiencies between 40 and 60%. This is still higher than vehicles with internal combustion engine (ICE) that generally have about 20%. [13]

$$\eta = \frac{\Delta G}{\Delta H} = \frac{237.34 \text{ kJ mol}^{-1}}{286.02 \text{ kJ mol}^{-1}} = 0.83 \quad (7)$$

2.2.2 Fuel Cell Vehicles

Fuel cell vehicles (FCVs), as well as electrical vehicles, could provide similar driving properties as vehicles with a regular ICE. The idea is to use hydrogen as a fuel to generate electricity from PEMFCs to power the wheels. Since the 1990ies, much research and development has been carried out by many automotive manufacturers. Most of the research has been focused on increasing the performance and in the same time reducing the size of the fuel cell stack. [14]

The hydrogen storage has also been a big struggle for the FCVs, due to the energy properties of hydrogen. The leading standard today is to compress the hydrogen and store it in a 70 MPa pressure tank. At this pressure, 5 kg of hydrogen is occupying a volume of 130 liters, which has an energy content that is enough to meet the expected driving range of 480 km. [14]

Toyota was the first manufacturer to release an FCV that is ready for mass production. The model is the Mirai, and uses Toyota's own developed fuel cell system. The Mirai is expected to be the breakthrough for the FCV market. [15]

2.2.3 Hydrogen Quality

The performance and durability of PEMFCs is strongly depending on the purity of the hydrogen. Various PEMFC related calculations and experiments are based on ultra-pure hydrogen gas, which means that the FCV manufacturers have put high demands on the purity of the commercial hydrogen gas. This has been accomplished by formulating a standard, ISO 14687-2:2012, which specifies which impurities that must be kept low to maintain performance and lifetime. [16]

The whole ISO 14687 has the general title "Hydrogen fuel – Product specification" and consists of three parts. The first part is about hydrogen specification for all types of applications, except those including PEMFCs. The latter applications have been moved to part 2 (for road vehicle application) and part 3 (for stationary application). Part 2 is the strictest specification, which means that if the hydrogen is pure enough for the ISO 14687-2, it will automatically be suitable for the other parts of the standard. [16]

The ISO 14687-2 presents a list of limiting characteristics which are the required specifications for hydrogen fuel quality (Appendix B). The focus of the work is: Proton exchange membrane catalyst and tolerance of the fuel cell components, effects of contaminants on the system, analytical considerations for different operations, onboard hydrogen storage and finally vehicle demonstration results. Currently this standard adapts to both hydrogen producers and filling stations. [16]

The specification contains 14 impurities that affect the fuel cell system in different or similar ways. The hydrogen gas should have a purity of at least 99.97%, which leave room for non-hydrogen gases up to a total of 300 ppm. It is especially important to keep the level of catalyst poisons low to maintain fuel cell lifetime. The full list of how the impurities affect the fuel cell system is seen in Table 2 below. [16]

| Impurity | A | B | C | Comment |
|--|----------|----------|----------|--|
| Water (H ₂ O) | X | X | | Ice formation in storage tank and potential for unwanted ion transport (K ⁺ and Na ⁺) |
| Total hydrocarbons | | X | | Adsorb to catalyst surface or preventing access to hydrogen. |
| Oxygen (O ₂) | X | | | Reacts with metal hydride storage material. |
| Helium (He) Nitrogen (N ₂) Argon (Ar) | | X | | Dilute the hydrogen resulting in affecting system operation and efficiency. |
| Carbon dioxide (CO ₂) | X | | | Affect storage tank with metal hydride alloys material. Reaction with water could result in carbon monoxide formation. |
| Carbon monoxide (CO) | | X | X | Reversible effect. |
| Total sulfur compounds | | X | X | Irreversible effect |
| Formaldehyde (HCHO) Formic acid (HCOOH) | | X | | Similar to carbon monoxide fuel cell performance degradation. |
| Ammonia (NH ₃) | | X | | Affecting the ion exchange capacity |
| Total halogenated compounds | | X | | Irreversible performance degradation |
| Particulates | | X | | Clogging of filters, valves and the fuel cell stack. |
| A: Onboard hydrogen storage B: Fuel cell performance C: Catalyst poison | | | | |

Table 2: Summary of the impurities effects on FCVs. [16]

3. Results

This chapter consists of two parts that are not directly associated to each other. Section 3.1 and 3.2 make up the first part and concern the purification aspects of the project. The second part is section 3.3 and 3.4 and describes the analytical aspects.

3.1 Purification Methods

Several hydrogen purification methods are either under development or available commercially in various scales and for different purposes. Table 3 is a list of typical techniques for hydrogen purification, summarized by Johnson Matthey Group Research Centre. The list has been used in this project for identifying candidates for the present application. [17]

| Technique | Typical feed | Product [%] | | Scale |
|--------------------------------|--|-------------|----------|-----------------|
| | | Purity | Recovery | |
| Cryogenic Separation | Off gases from petrochemical industries and refineries | 90-98 | 95 | Large |
| Polymer Membrane Diffusion | Off gases from refineries and ammonia purge gas | 92-98 | >85 | Small to large |
| Metal Hydride Separation | Ammonia purge gas | 99 | 75-95 | Small to medium |
| Solid Polymer Electrolyte cell | Hydrogen from thermochemical cycles | 99.8 | 95 | Small |
| Pressure Swing Adsorption | Any hydrogen rich gas | 99.999 | 70-85 | Large |
| Catalytic Purification | Hydrogen containing oxygen impurity | 99.999 | Up to 99 | Small to large |
| Palladium Membrane Diffusion | Any hydrogen containing gas | >99.9999 | Up to 99 | Small to medium |

Table 3: Brief comparison of hydrogen purification methods. [17]

The first four techniques in Table 3 are not able to purify the hydrogen to ultra-pure quality (99.999%). The cryogenic separation and polymer membrane diffusion have issues with impurities of CO₂ and water, which require further purification treatment. The metal hydride separation, that is available in medium scale, suffer from impurities like O₂, N₂, CO and sulfur which act as poisons to the hydrogen absorption. The solid polymer electrolyte cell is close to desired purity, but is not an option for the sodium chlorate process since it is only available in small scale. [17]

Remaining is the three techniques that are able to produce ultra-pure hydrogen. The catalytic purification is the same principle as the deoxo reactor described in the background section, which is already employed in some AkzoNobel facilities. This technique is excellent for reduction of oxygen and CO. However, other impurities are not affected to any larger extent. The process is also based on catalyzing chemical reactions rather than physically removing the impurities, which will result in a need for further purification steps. The pressure swing adsorption and palladium membrane diffusion techniques look promising for the purpose and are studied further below. [17]

3.1.1 Pressure Swing Adsorption

The separation mechanism in pressure swing adsorption (PSA) relies on that different gas species in a gas mixture interacts with the surface of specific solid materials during pressure regulation. These solid materials are called adsorbents, which can be packed in layers inside a vessel (more commonly associated with “bed”) to selectively adsorb impurities from an inlet gas feed at high pressure. The gas or gases less prone to adsorbing to the bed will exit on the top of the bed as a purified product stream. After some time, the adsorbents become saturated and the adsorption potential decreases. To achieve full adsorption potential again, the bed needs to undergo regeneration by depressurization and by purging using a pure hydrogen gas so the impurities desorbs from the adsorbents. Thus, the name *pressure swing adsorption* for the important changes in operation pressure. [18]

Theoretically, PSA is a batch process. In practice, at least two beds are used in parallel so that adsorption and desorption can take place simultaneously. However, a continuous product stream will not be obtained using a two-bed system, because it is favorable to use an

intermediate event to recover mechanical energy. This event is called equalization and is done by depressurizing the high-pressure bed and use the generated product stream to repressurize the low-pressure bed, until both beds have the same pressure. This invention enabled PSA manufacturers to economically scale-up to continuous purification by multi-beds systems. [19]

A minimum of four beds is required to obtain a continuous product flow, which has been of big interest for hydrogen producers. The four-bed PSA system is applied because each bed will perform one adsorption step and three regeneration steps. In the cycle, one bed will always perform the adsorption step, while the three other beds cooperate to attain the adsorption step again. In Table 4, the four steps that a bed will perform during a cycle are listed in chronological order. In each step, a total of three so called events could occur that are necessary for the system to operate cyclic. [19]

| Step | Events | | | Description |
|------|-----------------|---------|----------|---|
| A | Adsorption ↑ | | | High pressure adsorption and repressurization of D with parts of the product stream. |
| C | EQ1 ↑ | PP ↑ | EQ2 ↑ | Depressurization in three events; Equalization with D, providing purge (PP) to B and equalization with B after the purge. |
| B | BD ↓ | P ↓ | EQ2 ↓ | Depressurization by blowdown (BD) and purge (P) by the PP from C. Repressurization by equalization with C. |
| D | EQ1 ↓ | R ↓ | | Repressurization by the equalization step in C and the product stream from A. |

| | | | | | | | |
|------------|---------------------------|-----------|-----------------|----------|------------------|---|---------------|
| EQ1 | Equalization step 1 (C→D) | PP | Providing purge | P | Purge | ↑ | Upward flow |
| EQ2 | Equalization step 2 (C→B) | BD | Blowdown | R | Repressurization | ↓ | Downward flow |

Table 4: The four main steps each bed undergoes during a PSA cycle and a description of the nine included events. [19] The various colors are used for grouping similar events.

The cycle time varies from different manufacturers and inlet gases, typically about 10-30 minutes according to the bed size. In Figure 2, the pressure-temperature-diagram of a bed can be observed. [19]

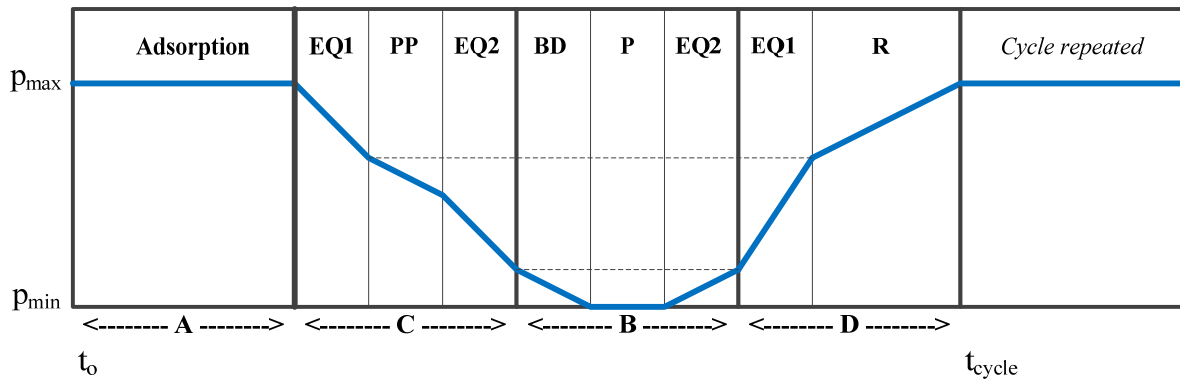


Figure 2: Pressure history of a bed undergoing the cycle. [19]

The beds are connected in a pipe and valve system, which makes it possible for every bed to perform all the events. In Figure 3, the four-bed PSA system is performing part I when the first bed is in adsorption mode. When the fourth bed has been fully repressurized, the valves are switched so that the gas flows to the part II setting, to enable the fourth bed to start adsorbing. Table 5, describes which steps each bed performs during each part of the cycle. The flowcharts of the whole PSA operation cycle can be found in Appendix C. [19]

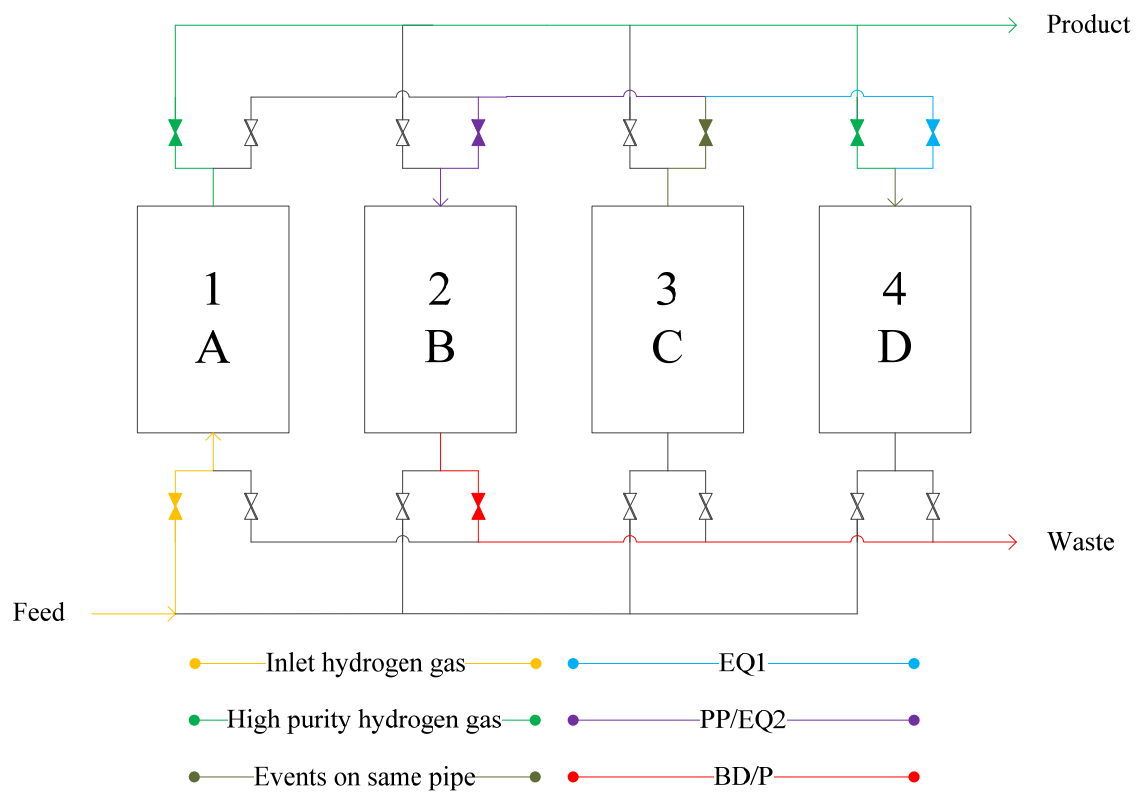


Figure 3: Flow charts of Part I of the four-bed PSA system operation cycle. [19]

| | | | | | | | | | | | | |
|-------|-----------------|---------|-----------------|----------|---------|-----------------|----------|----------|-----------------|----------|----------|--|
| Bed 1 | Adsorption ↑ | | | EQ1 ↑ | PP ↑ | EQ2 ↑ | BD ↓ | P ↓ | EQ2 ↓ | EQ1 ↓ | R ↓ | |
| Bed 2 | BD ↓ | P ↓ | EQ2 ↓ | EQ1 ↓ | R ↓ | Adsorption ↑ | | | EQ1 ↑ | PP ↑ | EQ2 ↑ | |
| Bed 3 | EQ1 ↑ | PP ↑ | EQ2 ↑ | BD ↓ | P ↓ | EQ2 ↓ | EQ1 ↓ | R ↓ | Adsorption ↑ | | | |
| Bed 4 | EQ1 ↓ | R ↓ | Adsorption ↑ | | | EQ1 ↑ | PP ↑ | EQ2 ↑ | BD ↓ | P ↓ | EQ2 ↓ | |
| Part | I | | | II | | | III | | | IV | | |

Table 5: The four parts (I-IV) in a cycle of a continuous four-bed PSA system. The beds current step (A-D) operation is presented in each part. [19]

Typically, commercial multi-bed PSA units are used for treating appropriate petrochemical off gases; mainly from steam reformers and oil refineries. When considering hydrogen gas from steam reformers, the feed to the PSA unit has already been pretreated with a catalytic step where the water-gas shift reaction occurs. Typically, the feed to the PSA unit contains 70 - 80% H₂, 15 - 25% CO₂, 3 - 6% CH₄, 1 - 3% CO and traces of N₂. [20]

Multi-bed PSA systems commonly consist of 4-12 beds, where the performance of the systems differ according to the number of equalization steps. Generally, a multi-bed PSA plant for hydrogen operates adiabatically at a temperature of 21 – 38 °C. The feed pressure is 4 - 30 atm, which also will be the maximum pressure of the product stream, whereas the waste gas stream will be collected at 1 - 1.7 atm. The purity of the product stream will be 98-99.999 mol% with a hydrogen recovery of 70 - 90%. The rather low hydrogen recovery is a result of the blowdown and purge events. [20]

Advantages with PSA systems in general are the flexibility, reliability and that the adsorbents are selective to several impurities at the same time. The disadvantages are the poor hydrogen recovery and the complex valve system that could cause stops. [20]

3.1.2 Palladium Membrane Diffusion

Palladium is a rare element that is important in membrane technologies for hydrogen purification thanks to its high selectivity and permeation rate. The idea of a palladium membrane is to let hydrogen be the only compound to diffuse through the membrane, which will result in an ultra-high pure hydrogen stream at the other side of the membrane. [21]

The gas separation mechanism is of the type *solution-diffusion* and can be described in six steps: [22]

1. *Adsorption*: Hydrogen molecules selectively adsorb to the surface of the membrane on the high pressure side.
2. *Dissociation*: The hydrogen molecules split into atomic hydrogen.
3. *Ionization*: The atomic hydrogen dissolves into the membrane lattice to protons and electrons.
4. *Diffusion*: The elementary components transfer through the membrane lattice.
5. *Recombination*: Protons and electrons recombine to atomic hydrogen at the end of the membrane and re-associate to form molecular hydrogen.
6. *Desorption*: The purified hydrogen desorbs from the membrane surface.

These six steps are illustrated in Figure 4.

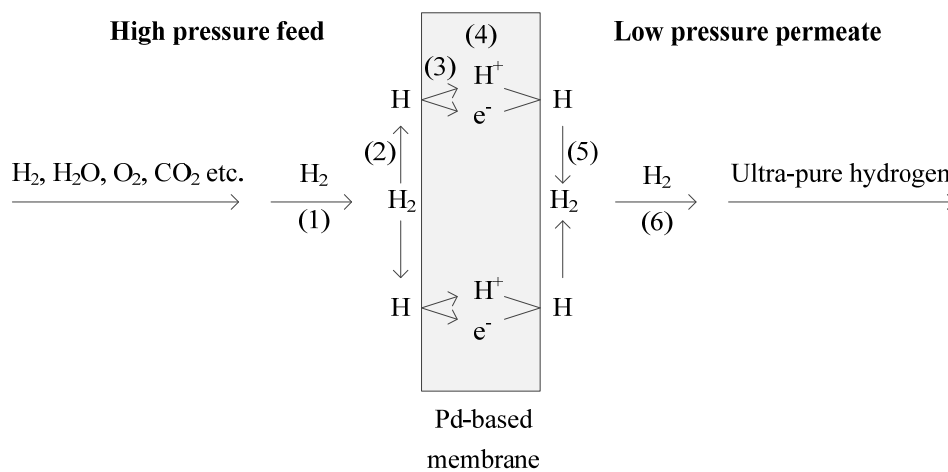


Figure 4: The solution-diffusion mechanism of permeation of hydrogen. [23]

Hydrogen flux, expressed in ($\text{mol m}^{-2} \text{s}^{-1}$), is a measurement of the hydrogen permeation rate through the membrane. The driving force for the flux is the difference in hydrogen partial pressure over the membrane. Moreover, hydrogen permeability and the membrane thickness affect the performance. For example, the hydrogen flux is inversely proportional to the thickness. This is the reason why palladium membranes need to be thin to achieve a high hydrogen flux. [21]

It is not favorable to use pure palladium as membrane for several reasons. Below 300 °C hydrogen embrittlement of the membrane might occur whereas temperatures above 450 °C might result in deactivation of the membrane by carbon compounds. Sulfur compounds cause irreversible poisoning of pure palladium membranes and the material cost rises with just using palladium. [24]

Instead of pure palladium, it is more feasible to use binary palladium alloys to achieve better membrane resistance and to reduce material cost. The permeability of the alloy is important when designing membranes. Table 6 shows the binary palladium alloys that have the highest permeability compared to pure palladium, according to experiments carried out by Knapton in 1977. [25]

| Alloy metal | | wt% of the alloy metal | Maximum normalized permeability ($P_{\text{alloy}}/P_{\text{Pd}}$) |
|------------------|-----------|------------------------|---|
| Yttrium | Y | 10 | 3.8 |
| Silver | Ag | 23 | 1.7 |
| Cesium | Ce | 7.7 | 1.6 |
| Copper | Cu | 40 | 1.1 |
| Gold | Au | 5 | 1.1 |
| <i>Palladium</i> | <i>Pd</i> | - | 1.0 |

Table 6: The weight percentage of palladium alloy metals to achieve the maximum permeability at the operating temperature of 350 °C. [25]

Palladium alloys with silver and copper are attractive to use in commercial membranes because of the comparably low material cost and high mechanical stability. Moreover, both alloys have shown enhanced resistance to sulfur compounds. The optimum amount of silver in the Pd-Ag alloy is limited to 23 wt% because the solubility of hydrogen increases and diffusivity decreases with higher silver content. The recommended Pd-Cu alloy composition has good permeability when considering the relative low palladium content. This good permeability is a result of high hydrogen diffusivity at 40 wt% Cu. The Pd-Cu alloy has also shown an even higher sulfur resistance than the Pd-Ag alloy. [25]

In order to increase the hydrogen flux and the mechanical strength of the membrane, composite support materials have been developed to enable a reduction of the palladium based membrane thickness. This has resulted in a classification of palladium membranes into three groups; unsupported, metal supported and ceramic supported. The supportive composites are placed between two thin layers of palladium, which means that the support material needs to have high hydrogen permeability. The porous stainless-steel-supported palladium membrane (PSS) is of the type metal supported membranes and is an attractive alternative thanks to its good mechanical properties. For example, it has a similar thermal expansion as palladium, which makes it suitable for processes with temperature cycling. [21]

Palladium membranes have mostly been limited to small scale laboratory set-ups. However, small to medium scale commercial units have been possible thanks to a patented Micro-Channel Technology from 2011. The feed gas passes through $\sim 300 \mu\text{m}$ wide channels inside vertically tubes, where the outer tube wall is the palladium membrane and the inner tube wall separates the feed gas from the outgoing impurity rich gas. The low pressure permeate side is located outside the tubes, which are surrounded by a chamber where the purified hydrogen can be collected. The palladium membrane uses the Pd-Cu or Pd-Ag alloy as separator and has a complex supporting construction. Figure 5 shows a schematic drawing of the inside of a tube applying this micro-channel technology. [26, 27]

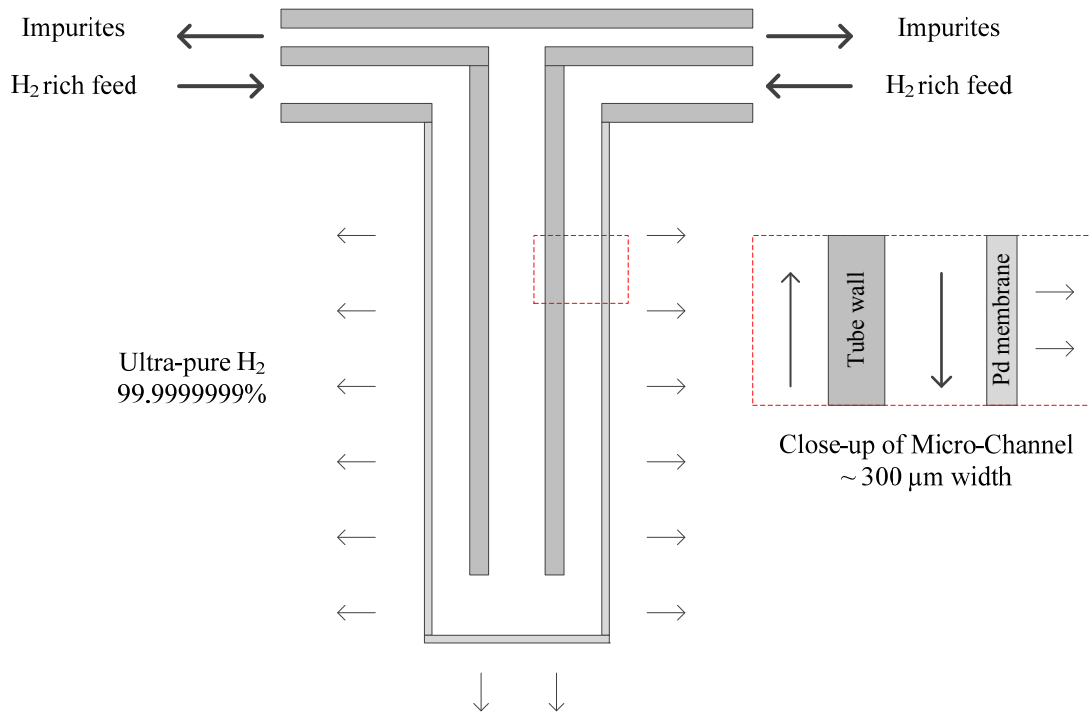


Figure 5: A vertical cross-section of a tube using the Micro-Channel Technology. [26]

An example of a manufacturer that applies the Micro-Channel Technology is SAES Pure Gas with their palladium hydrogen purifiers PD1 and PD2. The difference between the purifiers is that PD1 uses one cell and PD2 two cells in parallel. The two platforms together offer 44 different sizes, which give flow rates of 1-140 Nm³/h. According to the company, the permeate hydrogen will have a purity of 9N grade (99.9999999%), where the impurities O₂, H₂O, CO, CO₂, N₂, CH₄, non-methane hydrocarbons (NMHC), He and Ar have all been removed to a total concentration of <1 ppb. This is based on a feed gas with 99.99% purity, and a bleed of 2% of the maximum flow rate. The manufacturer claims that every impurity in a hydrogen rich gas stream can be removed and that the palladium membrane has an unlimited lifetime. [28, 29] However, an expectation of five years lifetime for palladium membrane is noticed in the literature. [30]

Large scale palladium membrane purifiers are currently not available due to several issues related to material and engineering design. Typically, the membranes cannot mechanically handle large flow rates and it is generally difficult to detect and eliminate defects in the membrane. The fabrication of the membrane is complicated and the high material costs also limits the scale-up possibilities. [31]

3.2 Proposed Hydrogen Purification Systems

In this section, potential hydrogen purification systems will be suggested for sodium chlorate facilities that could purify the hydrogen to meet the ISO 14687-2 standard. The basis is a sodium chlorate plant with an annual chlorate production of 50 kton, which co-generates approximately 4000 Nm³/h hydrogen. The plant uses a standard hydrogen purification system as described in the background section, i.e. a scrubber system followed by a carbon filter and a deoxo reactor. The hydrogen is assumed to contain the highest level of impurities as given in Table 1, which results in a purity of 99.7%. The deoxo reactor consumes 5% hydrogen during the formation of water, which means that 3800 Nm³/h purified hydrogen is available for further use. [10]

3.2.1 Full Production

If the plant usually uses small amounts of the produced hydrogen and vents the remaining hydrogen to the atmosphere, an installation of a multi-bed PSA system could be done to reach fuel cell graded hydrogen to sell. In Figure 6, a basic flowchart of the full production combination is shown. The material balance is based on the highest product purity at the lowest hydrogen recovery from section 3.1.1.

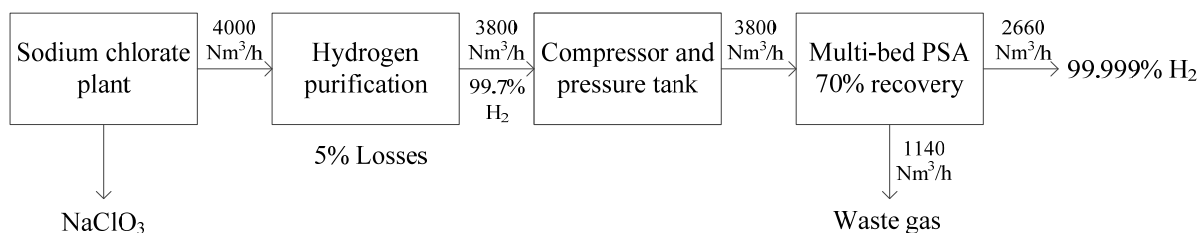


Figure 6: Concept of a multi-bed PSA system producing fuel cell graded hydrogen from the complete hydrogen flow from a 50 kton/y sodium chlorate plant. Flows given in Nm³/h of H₂

When determining the dimensions for the PSA beds, several factors regarding the feed and the desired output expectation have to be considered. Especially, the optimum number of beds is hard to determine. Typically, the primary factors to consider when estimating the number of beds are the hydrogen capacity and recovery, where the capacity is the starting point. The hydrogen recovery is depending on the target product purity and the pressure of

the purge gas. The product purity is not normally depending on the number of beds since each bed in a multi-bed PSA system should be observed as a separate batch processes, as described in section 3.1.1. The obtained product purity is rather depending on the amount of adsorbent material that furthermore is based on the feed flow and quality. [32]

In literature, hydrogen capacities below 5000 Nm³/h are usually classified as small capacities and four-bed PSA systems are normally used for petrochemical off gases. Moreover, high capacity systems above 50000 Nm³/h are using eight beds or more. [32] This is an indication that a four-bed PSA system may be most suitable for the setup in Figure 6. The impurities are assumed to not occupying any volume.

3.2.2 By-Production

If the plant already uses most of the generated hydrogen for other purposes, it is unnecessary to upgrade all hydrogen to fuel cell quality. Instead it is more favorable to split the hydrogen stream and further purify a small amount continuously or batch wise. Palladium membrane diffusion is a promising technique to ensure fuel cell graded hydrogen gas for smaller scales. Several manufacturers have been observed but it has been hard to find details on the used technology and capacity. SAES Pure gas purifiers have therefore been chosen as an example for this report. Figure 7 illustrates the setup when using SAES Pure gas palladium membrane purifier PS7-PD2-70, which is the one with highest capacity.

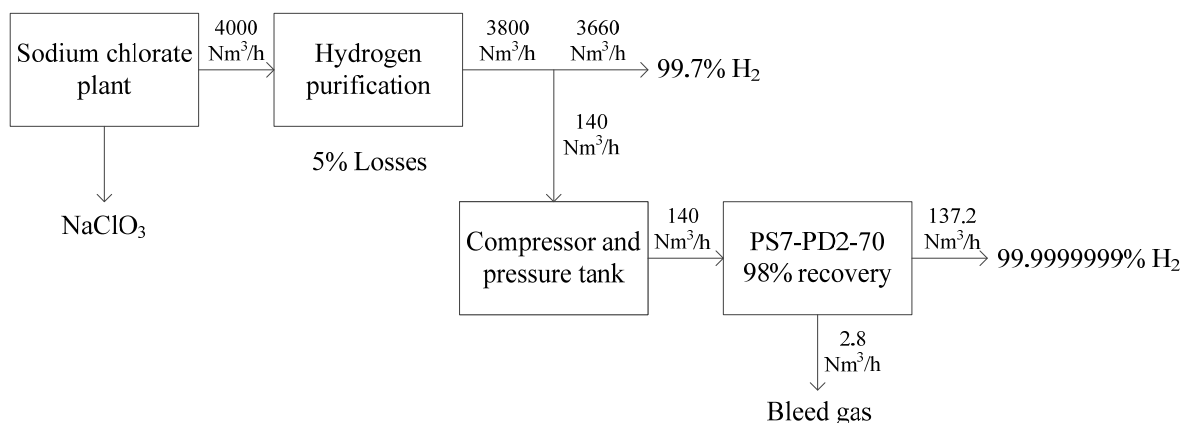


Figure 7: Concept of a palladium membrane system purifying a part of the generated hydrogen to fuel cell quality The PS7-PD2-70 is operating at maximum capacity.

The PS7-PD2-70 has a max inlet capacity of 140 Nm³/h, and can handle pressures up to 20.7 bar. The capacity strongly depends on the operation pressure, for example, when the purifier operates at an inlet pressure of 17.9 bar and an outlet pressure of 5.5 bar, the flow rate is reduced to 81.2 Nm³/h. The unit can be operated continuously and can, for example be equipped with an automatic N₂ purge system, and helium for leak testing. [28]

Another alternative for by-production of fuel cell graded hydrogen could be a two-bed PSA system. It would have similar performance as the four-bed unit described earlier, but tolerates low flow rates and is not continuous. [19]

3.3 Analysis Methods for the Impurities

The maximum limits of the fourteen impurities listed in the ISO 14687-2 have generally been set to relatively low values. Some of the impurities are set to extremely low values, like in the case of total sulfur compounds that needs to be lower than 4 ppb. This is the most challenging impurity to analyze and could in 2015 just be analyzed properly in top leading laboratories. [33] By the year 2017, all the member states of the European Union must ensure that the hydrogen refueling stations apply the technical specifications in ISO 14687-2. [34] This will put a lot of pressure on the companies in the fuel cell industry to provide recurrent analyses of the hydrogen.

3.3.1 Recommendation from ISO 14687-2

The standard has summarized suggested analysis methods that have been developed by National Physical Laboratory UK (NPL), ASTM International and Japanese Industrial Standards (JIS). All the analysis methods and their lowest detection limits are listed in Table 7. The analysis procedures are not included in the standard but can be found in the developers' external reports. [16]

| Impurity (max limit ppm) | Analysis method | Detection limit (ppm) |
|---|--|--|
| Water (5) | Dewpoint analyser GC-MS with jet pulse injection GC-MS with direct injection Vibrating quartz analyzer Electrostatic capacity type moisture meter FTIR Cavity ring-down spectroscopy | 0.5 1 0.8 0.02 0.04 0.12 or 1 0.01 |
| Total hydrocarbon (C1 basis) (2) | FID GC/FID FTIR | 0.1 0.01-0.1 0.01 |
| Oxygen (5) | Galvanic cell O ₂ meter GC-MS with jet pulse injection GC/PDHID GC/TCD Electrochemical Sensor | 0.01 1 0.006 3 0.1 |
| Helium (300) | GC/TCD GC-MS | 3-5 10 |
| Nitrogen, Argon (100) | GC-MS with jet pulse injection GC/TCD GC/PHID | 5 (N ₂), 1 (Ar) 1-3 0.001 |
| Carbon dioxide (2) | GC-MS with jet pulse injection GC/FID with methanizer GC/PDHID FTIR | 0.5 or 0.01 0.01 0.001 0.01 or 0.02 |
| Carbon monoxide (0.2) | GC/FID methanizer FTIR GC/PDHID | 0.01 0.01 or 0.1 0.001 |
| Total sulfur compounds (0.004) | IC with concentrator GC/SCD with concentrator GC/SCD without pre-concentration | 0.0001-0.001 0.00002 or 0.001 0.001 |
| Formaldehyde (0.01) | DNPH/HPLC GC/PDHID FTIR | 0.002-0.01 0.01 0.02 or 0.01 |
| Formic acid (0.2) | IC FTIR | 0.001-1 or 0.002-0.01 0.02 or 0.01 |
| Ammonia (0.1) | IC with concentrator FTIR | 0.001-0.01 0.02-0.01 |
| Total halogenated compounds (0.05) | IC with concentrator | 0.05 |
| Particulate concentration (1 mg/kg) | Gravimetric | 0.005 mg/kg |
| DNPH: Dinitrophenylhydrazine FID: Flame Ionization Detector FTIR: Fourier Transfer Infrared Spectroscopy GC: Gas Chromatography HPLC: High-Performance Liquid Chromatography IC: Ion-exclusion Chromatography MS: Mass Spectrometry PDHID: Pulsed Discharge Helium Ionization Detector SCD: Sulfur Chemiluminescence Detector TCD: Thermal Conductivity Detector | | |

Table 7: The suggested analysis methods including the lowest achievable detection limit for the impurities. [16]

Once the standard became accepted in 2014, it was well-known that there were knowledge gaps regarding the impurities' true effect on the fuel cell performance. As more knowledge is obtained, the requirements regarding hydrogen gas quality in the standard might therefore be adjusted [35]

Some specialists think that combining several impurities in an analysis of total content is a problematic move in the standard. The total halogenated compounds are one of the impurity groups on the list that has been claimed to be difficult to analyze properly. The halogenated compounds consist of organic, inorganic and diatomic compounds, where the physical and chemical characteristics differ significantly. It will be hard to develop an analysis method that is selective to all kinds of halogenated compounds. According to the literature, the analysis method currently proposed in the standard could have issues with selectivity for some halogenated compounds. [33]

3.3.2 Current State for Hydrogen Analyses in Practice

Many institutes and companies are interested in providing analytical services in relation to the ISO 14687-2 standard and a lot of research is performed for accuracy improvement and cost reduction. Several techniques for pre-concentrating the impurities by selective removal of hydrogen to a known factor are available. This gas enrichment will ensure that the low level impurities can be detected with higher detection limit. Therefore, the number of instruments will be reduced and the analyses will be more time effective. In the future when the number of hydrogen refueling points may have been increased, it will be important that on-line analysis methods are available to achieve analyses on-site instead of in laboratory. [36]

SP Technical Research Institute of Sweden (SP) is an example of an institute that is currently working with development of analysis methods in relation to the standard. In a report from 2015, SP shared the current state of the project. Table 8 is summarizing the detection limits that have been accomplished for each of the analysis methods. [37]

| Impurity (max limit ppm) | Analysis method | Detection limit (ppm) |
|--|---|----------------------------------|
| Water (5) | OFCEAS | 30 |
| Total hydrocarbon (C1 basis) (2) | GC/FID (2-5 carbon atoms) TD/GC/MS (>5 carbon atoms) | 2 |
| Oxygen (5) | GC/TCD (with He as carrier gas) | 30 |
| Helium (300) | GC/TCD (with H ₂ as carrier gas) | 300 |
| Nitrogen, Argon (100) | GC/TCD (with He as carrier gas) | 100 |
| Carbon dioxide (2) | GC/TCD (with He as carrier gas) | 2 |
| Carbon monoxide (0.2) | GC/TCD | 5 |
| Total sulfur compounds (0.004) | TD/GC/MS | 0.020 |
| Formaldehyde (0.01) | HPLC/UV-VIS (DNPH-cartridge) | 0.01 |
| Formic acid (0.2) | IC | 0.2 |
| Ammonia (0.1) | HPLC/Conductivity detector | 0.1 |
| Total halogenated compounds (0.05) | TD/GC/MS (excl. HCl and Cl ₂) | 0.05 |
| Particulate concentration (1 mg/kg) | - | - |
| <i>See Table 7 for acronyms</i> | | |
| OFCEAS: Optical feedback cavity-enhanced absorption spectroscopy | | |
| TD: Thermal desorption | | |

Table 8: Analysis methods including the lowest achievable detection limit for the impurities, developed by SP. The impurities with colored background are the ones that cannot be detected at low enough concentrations. [37]

SP has been able to analyze nine of the fourteen impurities, according to Table 8. Instruments for analyzing water and carbon monoxide are available at SP, but the detection limits are too high. For the other analysis methods that did not meet the standard, other instruments are required or more research and development needs to be applied. [37]

SP, together with other companies and different EU project groups are suggesting that the standard should be reformed in several ways. One of the biggest complaints has been that all the impurities must be analyzed, no matter where the hydrogen comes from. This have resulted in that companies needs to spend a lot of time and money on unnecessary analyses. One example of that is total halogenated compounds, which are quite common in chloralkali production but typically nonexistent in water electrolysis. [33, 38]

3.4 Hydrogen Sampling for the Analyses

It is important that the sampling of hydrogen is performed properly to avoid contaminants that could disturb the analysis results. The ISO 14687-2 standard recommends to collect one single large sample to complete all the analyses. If one sample is not enough, additional sampling needs to be performed at the same location under similar conditions. The sample container must undergo a repeated purge cycle before sampling to ensure that no residual gases are stuck inside the container. Safety is also an important factor, which means that the sample connectors must be approved. The standard refers to ASTM International examples of hydrogen sampling procedures. [16]

All the companies that perform hydrogen analysis have different policies for hydrogen sampling. SP will offer independent hydrogen sampling, as soon as the whole line-up of hydrogen analyses is complete. [38] VTT in Finland is also currently working on implementation of hydrogen analysis methods and will offer hydrogen sampling. AGA Gas in Sweden is known to perform hydrogen sampling, but it is unclear if they have or are working on developing analysis procedures for the ISO 14687-2. [10]

4. Discussion

The major findings of this project have been the identification of the two hydrogen purification methods PSA and palladium membrane diffusion. This was followed by how the methods could be integrated in the process and what the system could deliver in terms of quantity and quality. Finally, it was found that SP currently develops analysis methods for all the impurities in fuel cell graded hydrogen according to the ISO 14687-2 standard. SP is also planning to offer hydrogen sampling to customers, when the analysis methods are capable of detecting all the impurities with proper detection limits.

4.1 The Purification Aspect

In the case of PSA as purification method, literature indicates good bulk removal of impurities from petrochemical hydrogen off gases. The sodium chlorate by-product hydrogen is in comparison to petrochemical off gases relatively pure. The question is how a PSA system functions during upgrading of hydrogen rather than bulk recovery from gas mixtures. The chosen adsorbents would possibly deal with most of the impurities in Table 1 in section 2.1.2. However, oxygen and nitrogen could cause problems because of their high concentration and weak adsorption forces. In literature examples of PSA systems, the feed is normally completely free from oxygen and contains only traces of nitrogen. This could possibly mean that research on adsorbents with good selectivity to oxygen and nitrogen has been limited due to low demand.

The number of beds in a continuous PSA system is quite difficult to determine for the scenario in section 3.2.1 in terms of functionality. In petrochemical scale, four-bed PSA systems are recommended for capacities below 5000 Nm³/h hydrogen. A huge problem with this setup is that if a stoppage occurs in the PSA system, the sodium chlorate production needs to be shut down or the hydrogen after the main purification needs to be released to the atmosphere. If an eight-bed PSA system is used instead and a failure occurs in one bed, the valves could rearrange so that the hydrogen purification occurs just on a single four-bed line. Furthermore, the PSA bed dimensions and continuity needs to be investigated in a separate project to confirm that the system is able to purify enough hydrogen to fuel cell quality.

In the case of palladium membrane diffusion, the main advantage is that hydrogen is normally the only compound that could pass through the membrane. The effort of identifying adsorbents that is selective to some of the impurities that must be done when designing PSA units, is not needed because the palladium membrane can deal with all kinds of impurities in low amounts. The question is how the purity and recovery would be affected when considering sodium chlorate by-product hydrogen, with a total amount of up to about 2000 ppm impurities (Table 1).

SAES Pure Gas hydrogen purifiers, which are suggested as commercial alternatives in the results, can according to tests provide a hydrogen upgrade from 4N to 9N graded. In other words, the eight listed impurities that together had a concentration of 100 ppm have all been reduced to a total of <1 ppb. The total impurity concentration of the feed is noticeably lower than in the by-product hydrogen and even much lower than the maximum allowed total concentration stated in the ISO 14687-2 standard. It is hard to say whether SAES palladium membrane can handle these higher concentrations. It does not matter if the final purity proves to be either 4N or 9N as long as the total concentration does not exceed 300 ppm.

Using the largest SAES purifier with a capacity of ~140 Nm³/h seems to be good for the early state of a hydrogen infrastructure. The unit produces roughly 12.5 kg H₂/h, i.e. enough for about 2.5 FCVs/h assuming a tank capacity of 5 kg fuel. Hence, such a unit could supply e.g. a taxi firm with a fleet of 60 FCVs that refuels once every day.

Further work on the implementation of a purification system needs to be done. Apart from the design and demand aspect, perhaps some plant optimizing could be done in separate projects to reduce some impurity levels already in the existing process. It would, for example, be very beneficial if the nitrogen concentration was lower when applying a PSA unit. If the composed PSA system does not purify the hydrogen to fuel cell quality, palladium membrane techniques needs to be further researched in terms of mechanical strength and fabrication to resist higher flows. At the same time, a significant price reduction must occur for it to be considered in large scale applications.

4.2 The Analytical Aspect

Currently, the hydrogen analysis procedures constitute a large problem. Too many types of analysis instruments are needed to detect all the impurities and the validity is low for some impurities. At this state in Sweden for example, SP has a laboratory able to analyze most of the impurities (nine of fourteen), but the rest of the analyses must be carried out by state of the art gas laboratories in other countries. The current situation is neither economical nor practical, and requires that either the ISO 14687-2 standard is reformed in some aspects or that new analysis instruments are developed. Ideally, one or two instruments would be enough to analyze all impurities listed in the standard. With fewer instruments required to obtain a correct analysis, more laboratories would be able to offer sampling and analysis. Perhaps some large hydrogen producers could even invest in on-site laboratories and become independent of third party industries.

Hydrogen sampling in general does not seem to be problematic if it is done properly. It is up to the companies that have formulated their own sampling methods to guarantee that the sample is not contaminated. Otherwise, the standard has recommended sampling procedures that the companies could implement.

4.3 The Methodology Aspect

The limitation of excluding economic aspects when comparing purification methods is a relatively critical act. Palladium is expensive and the companies that provide commercial palladium membrane techniques sure spend much money on development and want to make money on their product. The price of the palladium purifier may not be justifiable in comparison to the limited hydrogen output, and it may therefore not be an optimal purification method for the purpose. More focus could have been applied on estimating future potential of the purification methods listed in Table 3, section 3.1. For example, polymer membrane diffusion might reach better purity and recovery in the future and become an attractive alternative for a sodium chlorate plant. In terms of the analytical aspects, it would be interesting to investigate further if the ISO 14687-2 standard is close to be reformed. SP's estimated time plan on their analysis methods development would also be interesting to find out.

5. Conclusions

Seven different types of hydrogen purification methods were compared with respect to purity, recovery and scale. Two purification methods were further studied;

- Pressure swing adsorption (PSA), works by adsorption of impurities during high pressure. Depending on the number of beds and equalization steps in the PSA cycle; an inlet feed of 70-80 mol% hydrogen can be purified to a level of 98-99.999 mol% hydrogen with a moderate hydrogen recovery of 70-90%.
- Palladium membrane diffusion, works by allowing only hydrogen from a hydrogen rich feed to permeate through the membrane. SAES Pure Gas are using the patented Micro-Channel Technology that enables flow rates up to 140 Nm³/h, where a 4N graded hydrogen inlet feed can be purified to a level of 9N. The hydrogen recovery is 98% according to the manufacturer.

Two different purification systems are suggested to work with sodium chlorate production;

- Full production: All of the hydrogen after the standard purification would be compressed and fed to a multi-bed PSA unit.
- By-production: A few hundred Nm³/h gas could be extracted from the main line after the standard purification. A SAES Pure Gas palladium purifier can be used.

The ISO 14687-2 standard, has suggested multiple analysis methods that could detect the impurities in hydrogen gas mixtures. Some impurities like total halogenated- and sulfur compounds are extremely difficult to analyze properly. There are companies and institutes developing own analysis methods. The Swedish technical institute SP has been able to analyze nine out of fourteen impurities correctly. SP will offer sampling to customers when all the analysis methods are ready. VTT and Aga Gas also have plans on providing hydrogen sampling in the future.

Further work with the hydrogen purification is to investigate how PSA and palladium membrane performs in practice with sodium chlorate hydrogen. Moreover, the public demand and the material economic aspects need to be considered when deciding which system that should be used. Hydrogen analyses and the standard would preferably be developed/reformed in several areas to suit a hydrogen infrastructure better.

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- [38] Daniel Braxenholm. (Daniel.Braxenholm@akzonobel.com) Subject: *SP work on ISO 14687-2*. Email to: Karine Arrhenius. (Karine.Arrhenius@sp.se) 2016-04-04

Appendix A – The Sodium Chlorate Process

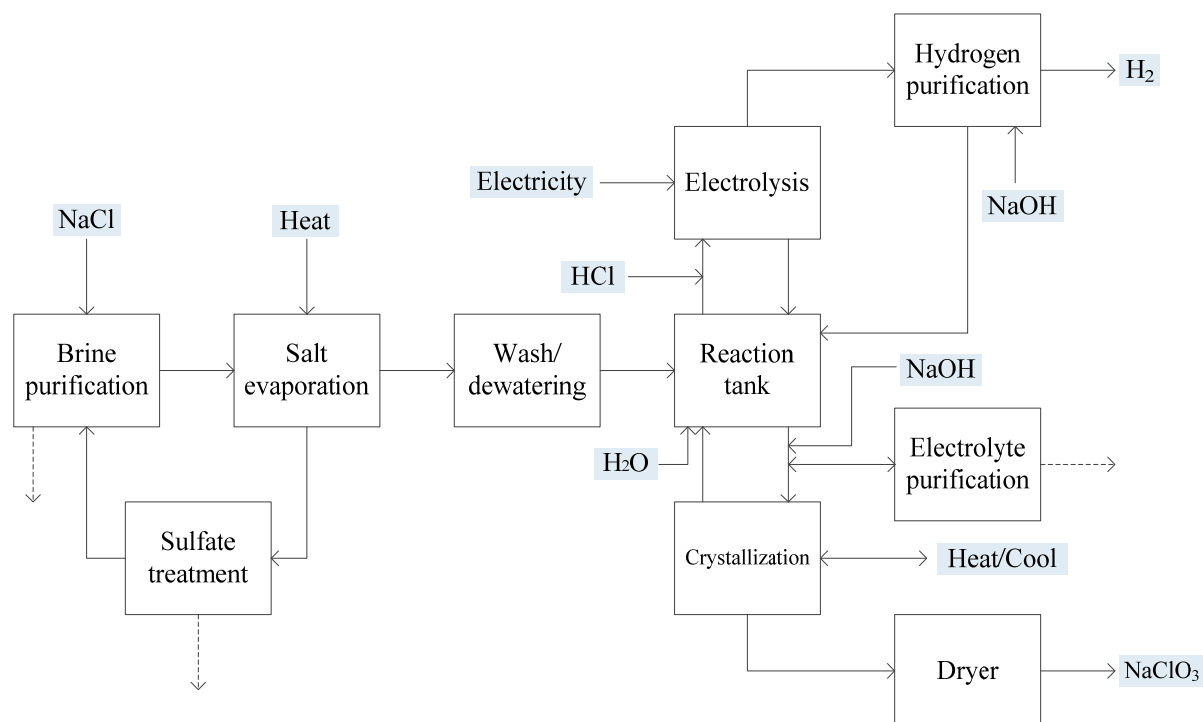


Figure A: An overview of the fundamental steps in the sodium chlorate process.

Brine treatment

The saturated brine solution produced by sodium chloride (NaCl) and hot water also contains impurities like calcium (Ca^{2+}), magnesium (Mg^{2+}) and sulfate (SO_4^{2-}). These are mainly removed in the brine purification. A final purification of the salt is obtained in the salt evaporation step where the salt is recrystallized before entering the electrolysis loop.

Electrolysis

The electrolysis loop consists of several electrolysis cells and reaction tanks where the reactions occur. Part of the electrolyte is taken to a crystallizer where sodium chlorate crystals are formed. The sodium chlorate formation requires pH regulation, which is served by adding hydrochloric acid (HCl) and sodium hydroxide (NaOH). In the electrolysis cells at the anode, chloride ions are oxidized to chlorine in acidic conditions as shown in Equation A1. The electrons transfer to the cathode where water, in alkali condition, generate hydrogen gas and hydroxide ions by reduction, see Equation A2. The hydrogen forms a gas phase that is taken to a hydrogen purification system.



The rapid hydrolysis reaction in Equation A3 is the reason why gaseous chlorine does not separate from the liquid phase. This reaction is a key feature for the sodium chlorate electrochemistry because the hydrolysis enables the formation of hypochlorous acid. Regulation of pH allows dissociation of the hypochlorous acid to sodium hypochlorite as presented in Equation A4. The final reaction of chlorate formation occurs both in the cells and reaction tanks in the pH range of 6-7, where the hypochlorite reacts with hypochlorous acid, according to Equation A5.



Crystallization

In the crystallization process, the formed sodium chlorate crystals will be separated and washed by filtration or centrifugation. The liquid filtrate (containing sodium chloride, sodium chlorate and sodium dichromate) is called mother liquor and recirculates back to the electrolysis loop. The sodium chlorate crystals need to be dried before entering the packing cistern. [10]

Appendix B – ISO 14687-2:2012

| Characteristics | Type I (grade D) Type II (grade D) |
|--|---------------------------------------|
| Hydrogen fuel index ^a | 99.97 % |
| Total non-hydrogen gases | 300 ppm |
| Maximum concentration of individual contaminants | |
| Water (H ₂ O) | 5 ppm |
| Total hydrocarbons ^b (Methane basis) | 2 ppm |
| Oxygen (O ₂) | 5 ppm |
| Helium (He) | 300 ppm |
| Total nitrogen (N ₂) and argon (Ar) ^b | 100 ppm |
| Carbon dioxide (CO ₂) | 2 ppm |
| Carbon monoxide (CO) | 0.2 ppm |
| Total sulfur compounds ^c (H ₂ S basis) | 0.004 ppm |
| Formaldehyde (HCHO) | 0.01 ppm |
| Formic acid (HCOOH) | 0.2 ppm |
| Ammonia (NH ₃) | 0.1 ppm |
| Total halogenated compounds ^d (halogenated ion basis) | 0.05 ppm |
| Maximum particulates concentration | 1 mg/kg |
| <p>Type I (grade D): Gaseous hydrogen fuel for PEM fuel cell road vehicle systems Type II (grade D): Liquid hydrogen fuel for PEM fuel cell road vehicle systems</p> <p>For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.</p> <p>a) The hydrogen fuel index is determined by subtracting the “total non-hydrogen gases” in this table, expressed in mole percent, from 100 mole percent.</p> <p>b) Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (μmolC/mol). Total hydrocarbons may exceed 2 μmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 μmol/mol.</p> <p>c) As a minimum, total sulphur compounds include H₂S, COS, CS₂ and mercaptans, which are typically found in natural gas.</p> <p>d) Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl₂), and organic halides (R-X).</p> | |

Appendix C – PSA Operation Cycle

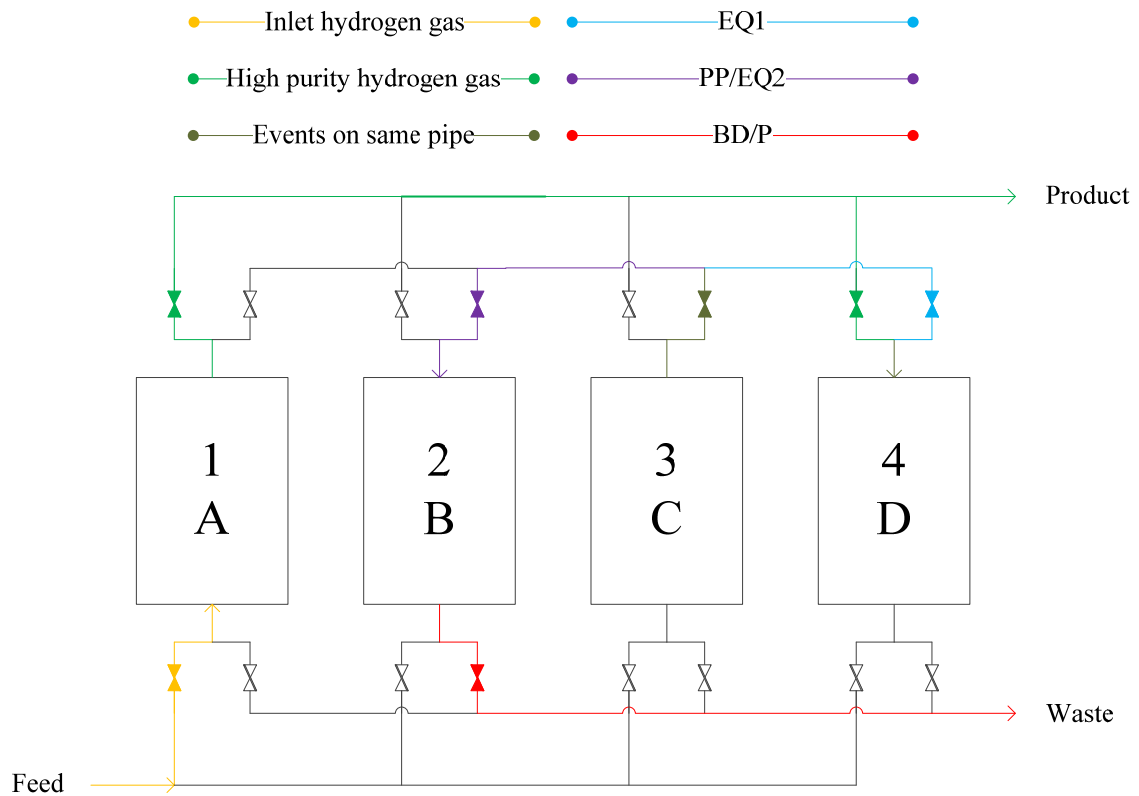


Figure C1: Part I in the four-bed PSA cycle

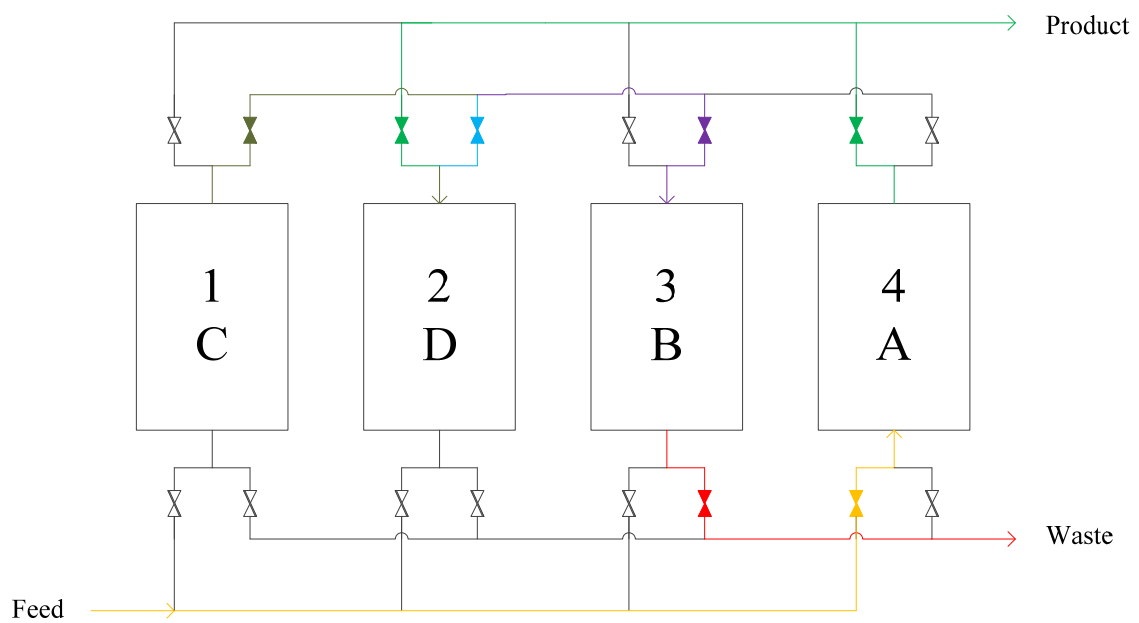


Figure C2: Part II in the four-bed PSA cycle

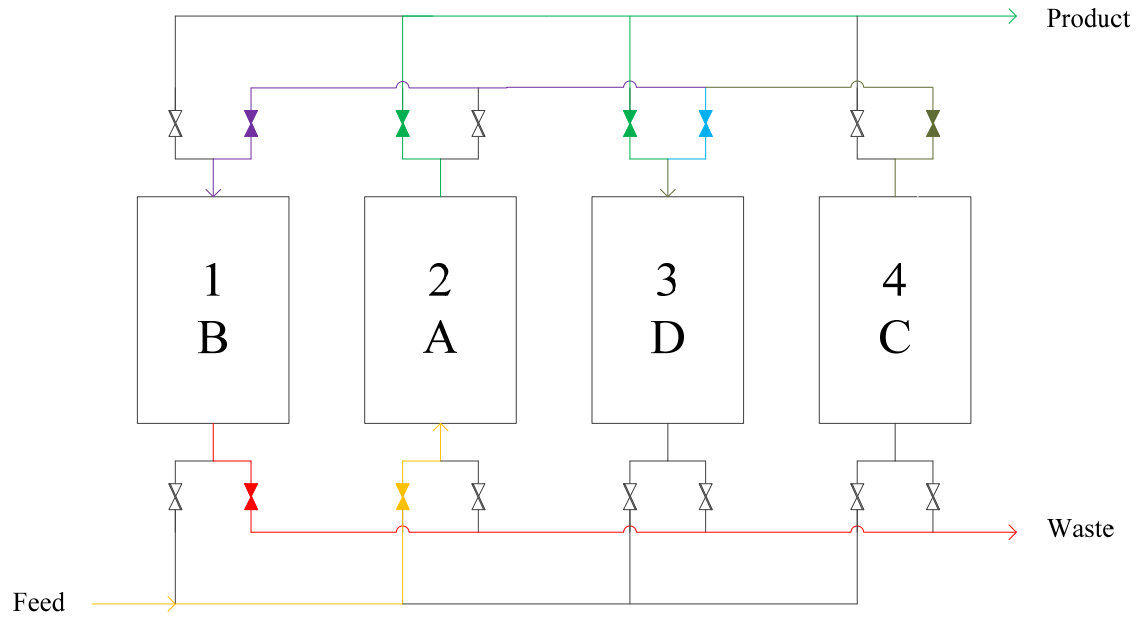


Figure C3: Part III in the four-bed PSA cycle

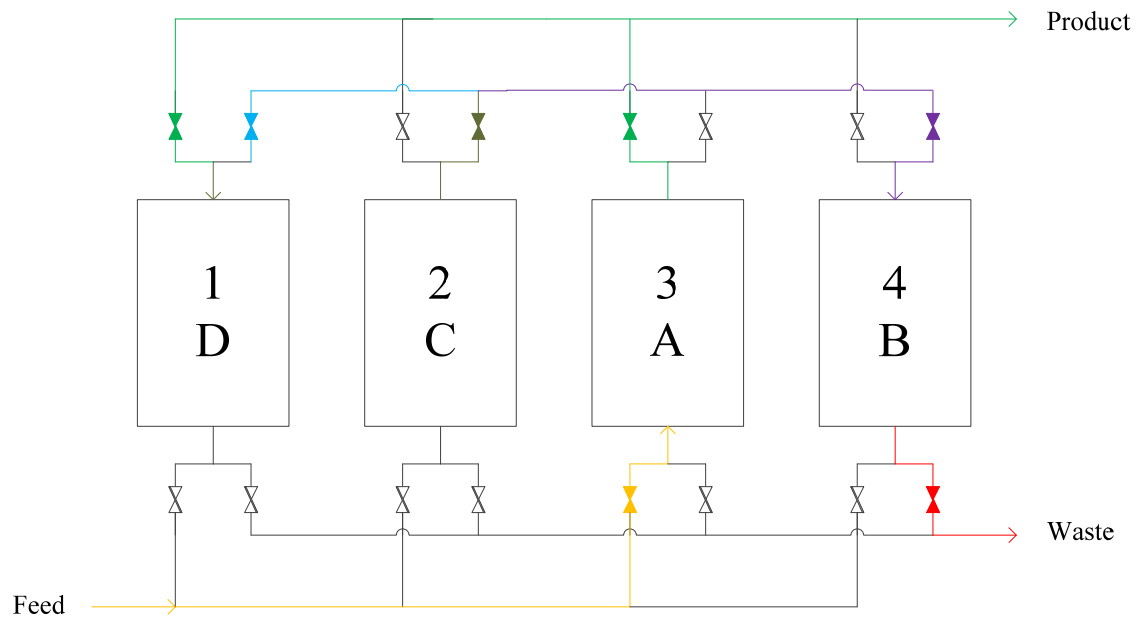


Figure C4: Part IV in the four-bed PSA cycle