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PRACTICAL OILFIELD APPLICATION OF HYDROGEN ELECTROLYSIS

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Abstract

The process discussed in this paper is a patent-pending system for generating hydrogen (H_2) utilizing oilfield produced water as feedstock. The process was designed to enhance and supplement existing oil and gas assets in Western Canada but can also use seawater and other brines.

The process (referred to as Dynamic Brine Electrolyzer or "DBE" in this paper) will be of primary interest to upstream Oil & Gas Producers interested in reducing their carbon emission intensity (CI) and extending the economic lives of certain assets.

One of the distinct advantages of this particular process is the direct utilization of seawater to generate hydrogen. This is possible primarily through the usage of a membrane-free bipolar brine. Further, in contrast to many other electrolyzers, the design of this unit employs the flow of water in a two-step process, to allow for the liberation of hydrogen and oxygen at two distinctly different locations as connected by this flow of water between them (hence the term 'Dynamic' in the name).

The current DBE iteration employs equipment presently available on the market, utilizing the training and experience of Western Canada's current crop of oilfield workers. Combined with balance-of-plant savings not seen with other electrolyzer offerings, the DBE system is expected to provide competitive hydrogen from the upstream Oil & Gas (O&G) sector.

Resistance to the effects of oil, sour and hard water components have been addressed by the DBE. Also, plant expansion and component change-out is readily and efficiently carried out on-line, due to the DBE's modular design.

Target hydrogen costs for this unit are expected to fall between those of Blue and (currently) Conventional Green Hydrogen. This technology can act as a "battery" for solar and wind installations and, as such, there is strong support for the DBE from renewable energy developers in Western Canada.

At the time of this paper (summer 2023), AH2 is actively testing their design in the Exergy labs in Quarry Park, Calgary, Canada.

Introduction

Investors and Governments are all actively promoting Blue and Green Hydrogen generation, however, both Blue and Green Hydrogen require de-ionized water, and for some processes (e.g., Steam Methane Reforming), the volume of pure water required can be quite substantial.

The Western Canadian Basin has limited fresh water, but significant brine reserves. In addition, the Western Canadian Basin has a large and robust Oil & Gas (O&G) infrastructure.

This paper focuses on the electrolysis of brine, specifically oilfield produced water, as a promising and sustainable approach for hydrogen production. The principle, advantages, challenges, and future prospects of the Dynamic Brine Electrolyzer (DBE) route in the context of hydrogen generation are discussed herein.

Principle of the Dynamic Brine Electrolyzer

The Dynamic Brine Electrolyzer (DBE) is a two-step process.

For Step 1, hydrogen is generated within the DBE in the same manner as hydrogen is generated within Polymer Electrolyte Membrane (PEM) or alkaline electrolyzers:

Cathode (reduction) $$2H_2O + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$$

However, the half reaction at the anode is quite different, as unlike PEM or alkaline units, no oxygen is produced by the DBE anode:

Anode (oxidation) $$2Cl^- \longrightarrow Cl_{2(aq)} + 2e^-$$

This alternative half reaction occurs at the DBE anode because of the (counterintuitive) higher electronegativity of oxygen versus chlorine.

Dissolved chlorine is produced preferentially from the brine electrolyte of the DBE, as opposed to the oxygen gas that comes from pure water splitting by PEM and alkaline electrolyzers.

For reference; at atmospheric pressure and the temperatures typical of the DBE, about 7g of chlorine dissolve in one litre of water versus the corresponding solubility of oxygen at about 0.04g/l and hydrogen at about 0.0015 g/l.

Meanwhile within the DBE electrolytic cell, under the controlled electrolyte conditions of Step 1, any dissolved chlorine gas is rapidly converted via a disproportionation redox reaction to hypochlorite:

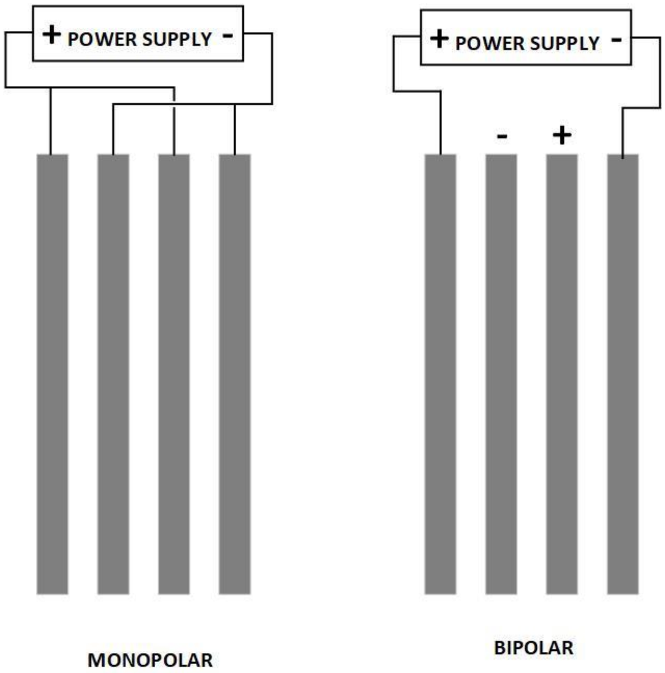
$$Cl_{2(aq)} + OH_{-(aq)} \longrightarrow OCl^-_{(aq)} + Cl^-_{(aq)} + H^+_{(aq)}$$

For Step 2 of the DBE process, the electrolyte proceeds to a reactor, which is also under control, but at new and different conditions. At the Step 2 reactor, oxygen gas and chlorine ion are generated:

$$2OCl^-_{(aq)} \longrightarrow O_{2(g)} + 2Cl^-_{(aq)}$$

As shown in Figure 1, Step 1 of the current version of the DBE employs bipolar cells. Bipolar refers to the method of delivery of electricity to the cells and is a common feature of various electrolyzers. Bipolar electrodes employ induction, while monopolar electrodes are directly connected to the power supply. Bipolar design simplifies construction and maintenance.

Figure 1: Monopolar vs Bipolar Electrolyzer Configurations



As discussed below, DBE bipolar cells do not contain a membrane or diaphragm between electrodes per other electrolyzers. This further simplifies electrolyzer construction for the DBE.

The following sketch (Figure 2) illustrates the DBE concept. Typically, in an upstream O&G facility, water is produced as a byproduct of hydrocarbon production. This water is collected in a "Produced Water" tank and injected into a well to dispose of it sustainably and/or to help maintain hydrocarbon production by returning the produced water to the producing reservoir.

The DBE will typically be a retrofit to such an existing facility, employing the existing infrastructure and utilities (such as instrument air and low-grade waste heat). If required, because of excessive scaling components in the water, ion exchange or lime softening may be needed.

AH2 is currently working in the lab on another method of scale mitigation that also has the potential for significant carbon sequestration.

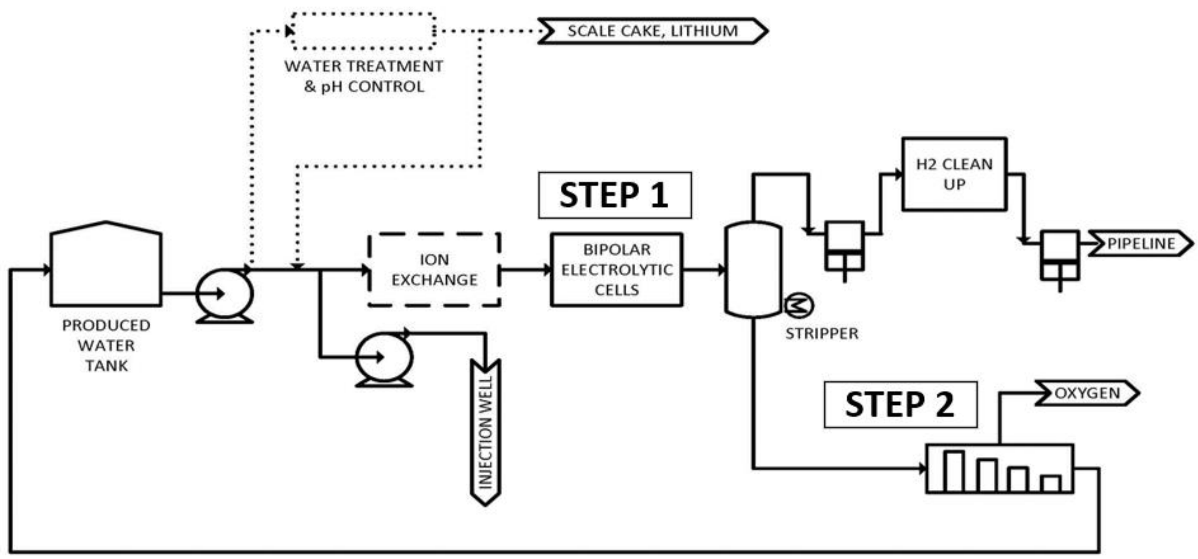
Referring again to Figure 2, below, after Step 1 and before Step 2, it is necessary to remove the hydrogen from the water stream to segregate the H_2 product of Step 1 from the O2 that will be generated downstream in Step 2.

Step 2 releases O2 gas and chloride ion. The brine solution resulting from Step 2 can then be returned to the Produced Water Tank.

Hydrogen clean-up will likely employ Pressure Swing Adsorption (PSA), much like other Blue and Green Hydrogen production units.

Conceivably, by increasing pump discharge pressure in Step 1, it should be possible to remove one or more stages of the hydrogen compression downstream of the stripper column identified in Figure 2.

Figure 2: Dynamic Brine Electrolyser Block Flow Diagram



Because of the wide variation seen in produced water concentration from various producing zones, the ensuing resistivity of the produced water can likewise vary considerably. Accordingly, for our proposed polymer-based electrodes, we are also examining varying electrode separation to allow for local chloride concentration.

Figure 3: Resistivity of NaCl Solutions

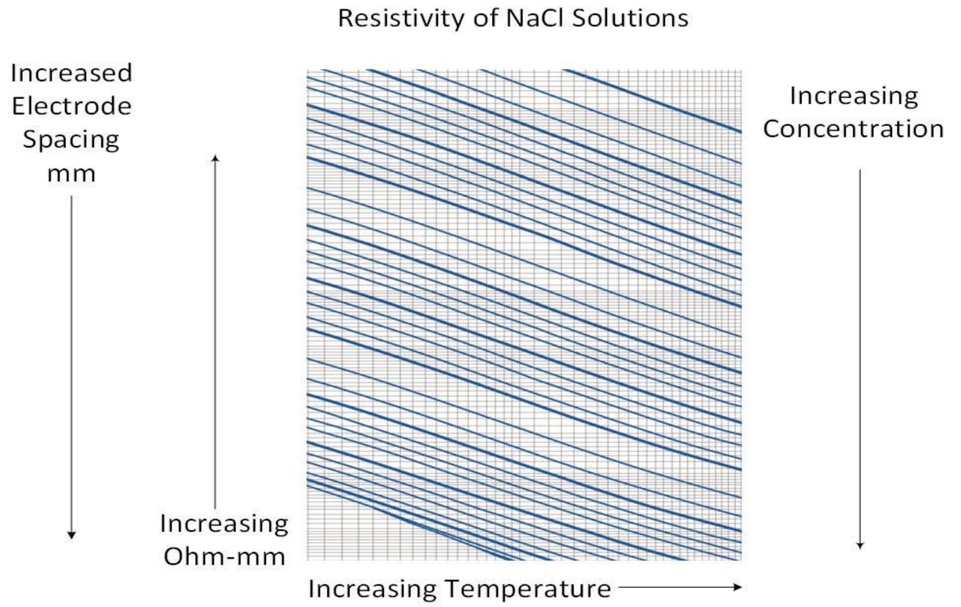


Figure 3 illustrates a number of factors (but not all), that affect the efficiency of the electrolysis process. Other factors include temperature and pressure. Based on all of these factors, an "anticipated" efficiency for the DBE is expected as follows:

Expected Experimental Results (per the Literature)

Purity	~95% H_2
Hydrogen Power Needs	~50 kW/kg*

Actual values cannot be released prior to granting of patent and completion of lab studies.

**Note: as stated above, there are many factors that affect the efficiency of hydrogen generation. Best current practices are reaching efficiencies in the range of 70 to 80%, which is how the above was estimated for the Alberta H2 DBE. For more information on hydrogen electrolysis efficiency, explore available references (some cited at the end of this paper).*

Advantages of the Dynamic Brine Electrolyzer

Commercial Polymer Electrolyte Membrane (PEM) electrolyzers employ membranes and commercial alkaline electrolyzers employ diaphragms to separate the H2 from the O2 produced in the electrolyzer cell. O2 must be physically separated from hydrogen in these designs for hydrogen product purity and for obvious safety reasons.

The AH2 Dynamic Brine Electrolyzer (DBE) has no physical barrier between the cathode and anode because hydrogen gas is generated within the electrolytic cell along with little to no other gas. Oxygen generation occurs downstream at a different location. This configuration, as described above, results in a much simpler construction for the DBE than other electrolyzers.

The spacing between anode and cathode for hydrogen generation in electrolyzers can be of the order of 3 mm to avoid excessive power draw.

In contrast to the DBE, for example, the PEM electrolyzer requires placing a membrane between plates that are 3 mm apart, plus allowing for electrical connections, while providing for the passage of water and gas, as well. This represents quite an arduous manufacturing endeavour on the part of the PEM unit.

For both the alkaline and PEM electrolyzers, oxygen bubbles interfere with operation of the anode because these bubbles tend to "stick" to the anode and block effective electrical connectivity between the anode and the electrolyte. Because only hydrogen gas is generated by the DBE cell, problematic oxygen gas bubble generation at the anode is avoided and the DBE does not experience this difficulty.

The various membranes and diaphragms employed by PEM and alkaline electrolyzers are typically composed of challenging Per and Polyfluoroalkyl Substances (PFAS). These are the so-called 'forever' chemicals that are currently the subject of proposed bans in the European Union and elsewhere. The DBE does not employ PFAS.

As stated above, the need for physical O2/H2 separation between the electrodes of other electrolyzers presents significant construction challenges. This factor also introduces maintenance and possibly operational difficulties not experienced by the DBE.

For example, the tight tolerances seen in PEM and alkaline electrolyzers do not provide much room for error during operation. Further, electrodes and or membranes/diaphragms require periodic repair or change out. Tear down of these devices requires OEM support and may not be possible on-site.

DBE has relatively loose tolerances and it is designed around site repair and maintenance. As such, the DBE has much reduced water treatment requirements and fewer maintenance concerns than these other electrolyzers.

In addition, if and when required, teardown of single DBE modules is relatively easy, allowing for rapid and radical cleaning, as well as providing for ease of component repair or replacement. Further, because of its modularized design concept, the DBE can be configured for online repair and online system expansion.

Using produced water, scale deposition on the electrodes of the DBE is a constant issue. When scale is deposited on the electrolyzer electrodes or elsewhere, it is mitigated by employing scale buffering agents, such as CO_2 and daily removal using reverse polarity.

Reverse polarity is not available to other hydrogen generating electrolyzers because of the need to physically segregate oxygen from hydrogen in these other devices.

Further, another property, polarization of the electrolyte at the electrodes can be an issue with electrolyzers. Polarization is a “layering” of charged particles, whereby, for instance, positive particles (e.g., hydrogen and sodium ions) line up against the negative electrode.

This positive layer causes negative particles (e.g., chloride and hydroxide) to line up behind the positive layer, which, in turn induces another positive layer and so on and so forth.

Polarization increases local electrical resistance within the electrolyte. Reverse polarity depolarizes the DBE electrodes, reducing power consumption.

Another benefit seen with the DBE design is that oil deposition on the electrodes appears to be mitigated by the same procedures that are employed for scale inhibition (reverse polarization and solution buffering). This is because of the surface charges present on oil droplets and suspended solids (so-called ‘zeta potential’).

Sour components in the produced water are removed from the produced water stream by cycling a small amount of one of the DBE internal streams ahead of the DBE, thereby precipitating solid sulphur for removal by deposition in the Produced Water Tank or via filtration.

The DBE does not involve any new science. As presently arranged, it uses readily available commercial equipment, reconfigured for hydrogen generation.

The design employs equipment currently available on the market, utilizing the training and experience of Western Canada’s current crop of oilfield workers. Combined with balance-of-plant savings not seen with other electrolyzer offerings, the DBE is expected to provide competitive hydrogen from the upstream O&G sector. In addition, it may have important seawater or similar brine applications as well.

Resistance to the effects of oil, as well as sour and hard water components have been addressed by this design. Appropriately organized, component change-out can be readily and efficiently carried out on-line.

Challenges and Limitations

1. Large water flowrates are required for the current process.
2. In common with other electrolyzers, dedicated on-site electrical power generation (for the purpose of hydrogen generation) may be more economically attractive than grid power used for the same purpose.
3. For brine containing high levels of scaling agents, a weak acid ion exchange or other water treatment measure may be required.
4. At high pressure, unacceptable concentrations of dissolved hydrogen or oxygen may be present in the water to be returned to the reservoir.
5. The DBE has a tight operating range for temperature, the voltage applied to its electrodes and in terms of the chemical tuning required to simultaneously promote acceptable production, while discouraging unwanted byproducts.
6. The environment of the DBE is inherently corrosive, and as such, special materials, such as HDPE liners must be employed.
7. Step 2 puts an upper limit on OCl^- concentration and is very pH sensitive.

Future Perspectives and Research Directions

AH2's current DBE test unit:

- Operates at about 14 psig (100 kPa). The intent is to increase this to about 400 psig to lower H_2 compression needs, in line with current commercial electrolyzers.
- Employs commercial, bipolar Mixed Metal Oxide (MMO) electrodes on titanium sheets. We plan to test inexpensive polymer-based electrodes that have the potential to significantly reduce CAPEX and OPEX.
- Is based upon DC electricity. Because of the design of our electrolyzer cell, it may be possible to employ AC current, potentially reducing scaling and electrode polarization (reducing or halting electrical efficiency losses), while minimizing electrical CAPEX and OPEX in some situations.

The use of CO_2 for water softening, permanent CO_2 sequestration and as well, relatively pure O_2 generation (and on-site usage) in concert with DBE operation should be evaluated.

Conclusion

The Dynamic Brine Electrolyzer offers a sustainable approach for hydrogen production, leveraging the abundant resources of Western Canada (and other similar environments). Its potential advantages, such as cost-effectiveness, scalability, and compatibility with renewable energy sources, make it an attractive alternative to other methods of making hydrogen. However, addressing the associated challenges and further exploring research directions are crucial for successful implementation. This will require innovative approaches and possibly additional collaborations.

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