

Energy Production From Hydrogen Co-Generated In Chlor-Alkali Plants By The Means Of Pem Fuel Cells Systems

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The main goal of this project is to produce electricity with the hydrogen co-generated in the electrolytic process for chlor-alkali production: if used within the same plant, this energy reduces the electricity consumption from the main supply up to 20% of the needed amount, thus optimising plant energy efficiency.

In this particular respect, fuel cells represent a valid energy production device since they can be fed from the anode side with the hydrogen already available at the plant and, from the cathode side, with environmental air.

Fuel cells convert the chemical energy of the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ directly into electricity, thereby avoiding the thermodynamic limitations that are typical of thermal generators and achieving net efficiencies of more than 50%.

The DC electricity that is produced can be easily converted into higher current and lower voltage electricity by the means of a DC/DC regulator and sent back to the electrolyser, allowing energy consumption savings up to 20% of plant demand.

In addition to that, the chemical reaction between hydrogen and oxygen is transformed into electricity without producing any combustion derivatives since the only final products involved are pure water and heat, therefore resulting beneficial also for environmental purposes.

Furthermore, fuel cells are installed where hydrogen is already available and the standard procedures and regulations relating to the use of this gas are already known and applied: this guarantees the total compatibility of the fuel cell device with the equipment already in place.

As industrial size examples, the presentation will illustrate the 120 kW pilot plant already installed at a chlorate production site in Italy and, as a showcase, the technical and economical feasibility study for a 2 MW plant.

1. Foreword

Using fuel cells for recovering hydrogen from industrial processes (with specific reference to the chlor-alkali and sodium chlorate industry) is one of the most innovative energy applications as it fits with indications given by international workgroups involved in developing the economy of hydrogen for producing clean electricity.

In fact, fuel cells can be fed with hydrogen that exceeds chlor-alkali plants current usage (compression and sale, raw material for producing chemicals) in order to produce electricity to be reused in the cell room.

In this respect Uhdnora and Nuvera are linked since February 2005 for developing and marketing PEM (Proton Exchange Membrane) fuel cells based systems (whose trade name is FORZA) specifically designed for electro-chemical plants.

1.1 Basic data for the chlor-alkali (C/A) plant

1.1.1 The reaction

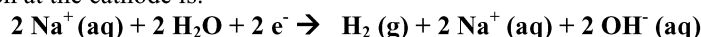
The main principle for the electrolysis of an aqueous solution of a chloride is as follows:

- The chlorine ions (Cl⁻) are oxidised at the anode to form chlorine gas (Cl₂).
- At the cathode: if mercury is used an Na/Hg amalgam is formed and then hydrogen (H₂), and hydroxyl ions (OH⁻) are formed by adding water to the decomposer.

The reaction at the anode is:



The reaction at the cathode is:



The total reaction is:



Electrolytic hydrogen is very pure and it can be used for organic hydrogenation, catalytic reductions, ammonia synthesis and to provide hot flames or protective atmospheres in welding technology, metallurgy or glass manufacture. It is also widely used in the manufacture of high-purity hydrogen chloride (HCl).

Most of chlor-alkali and sodium chlorate producers have got an excess of hydrogen, which is usually burned as a fuel for heating and drying: this hydrogen could be better valorised for instance by feeding a fuel cells power plant.

1.1.2 The technology

There are three electrolytic chlorine/NaOH/H₂ production processes: mercury, diaphragm, membrane (see Figure 1). In particular, the membrane chlor-alkali process is state of the art technology.

Electric power consumption is a very important parameter for chlor-alkali production economics and it is determined by current efficiency and cell voltage (refer to Fig.1). Not surprisingly, producers have always worked actively to reduce energy consumption since it represents up to 70% of the variable cost of production.

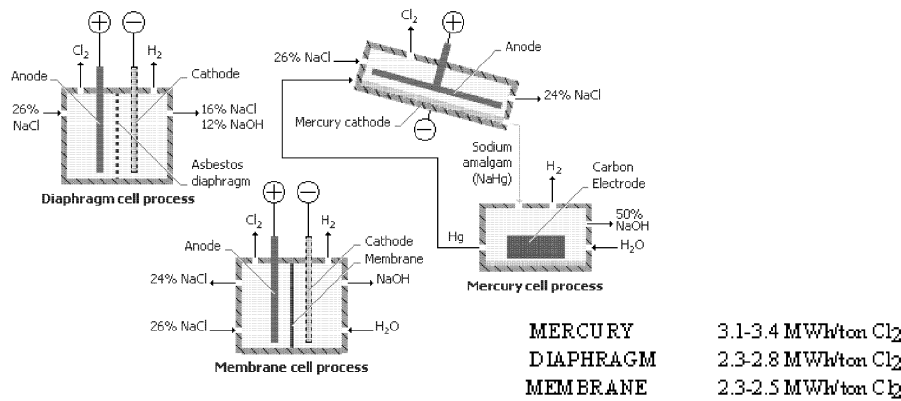


Figure 1 (Source: Wikipedia – www.wikipedia.org)

1.2 Working principle of PEM fuel cell technology

A fuel cell is an electrochemical device that transforms thermodynamic energy into direct current (DC) electricity that can be used to power any electric device.

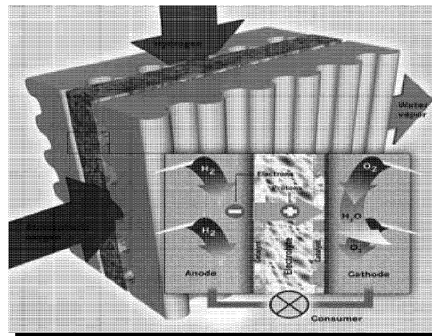
More specifically, a “PEM” or “proton exchange membrane” fuel cell is made up of two electrodes, an anode and a cathode, separated by a solid electrolyte and made up of a thin polymer membrane that only allows H^+ protons to move from the anode to the cathode.

The anode is fed with (pure) hydrogen that is separated into protons and electrons by a catalyser. At this point, while the protons migrate towards the cathode through the polymer membrane, the electrons that cannot pass through the membrane reach the cathode via an external circuit, thereby generating an electric current.

Meanwhile, the cathode receives oxygen (contained in the air) and a catalyser (typically platinum) allows it to recombine with the protons coming from the membrane and the electrons from the external circuit, thus forming water according to the reaction shown in the diagram (see Figure 2).

Figure 2. PEM fuel Cell Technology: how it Works

- Transforms hydrogen and oxygen into electricity without combustion
- Fully scalable with high efficiency at every power size
- No moving parts inside the fuel cell
- Only by products are water and heat



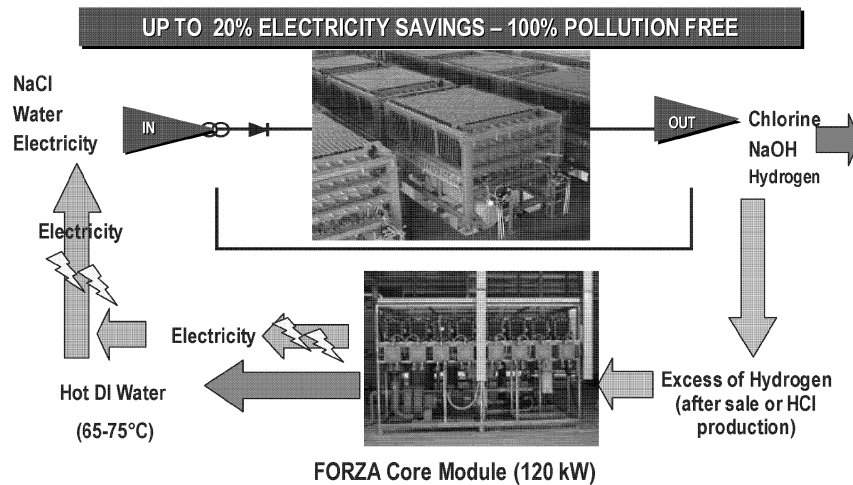
Membrane Electrode Assembly

The electrochemical reaction in a fuel cell is cleaner and more efficient (>50%) than the combustion reaction that occurs in an IC engine (mostly around 30%).

2 Description of the 120 kW pilot plant and working conditions

The way the FORZA™ core module operates is described in Figure 3.

Figure 3: FORZA™ applied to C/A process- Working principle



Installation on C/A plants is covered by a Nuvera patent: "Method for the integration of fuel cells into electrochemical plants", Pat.No 6,423,203 B1 Dated Jul 23,2002

2.1 The 120 kW FORZA™ pilot plant installation

The 120 kW pilot system was first checked by Nuvera and Uhdenora at the industrial laboratories set up at SIAD-Praxair premises in Osio (Bergamo).

Then, in order to validate the technology, the system was installed at Caffaro premises (Brescia), where it was connected to the electrolyzers for sodium chlorate production (see Figure 4) in order to work with "industrial" quality hydrogen produced by this unit: the pilot system worked unattended 24/24h - 7/7days from September 2006 to December 2006 for approximately 2500 hours

Figure 5 shows the MCC and the energy conversion device (DC/DC converter).

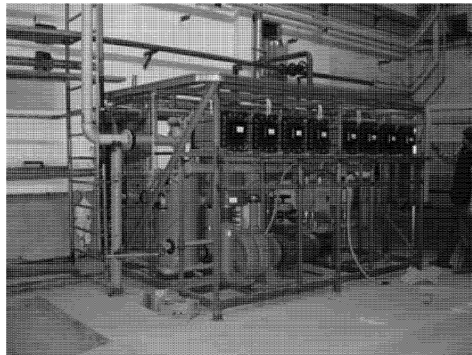


Figure 4

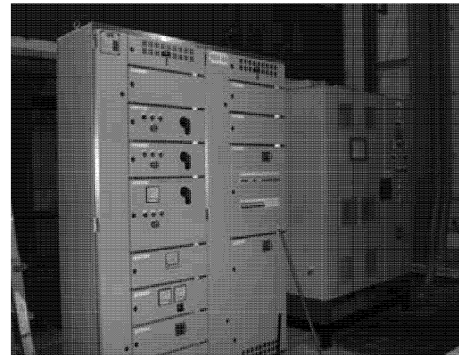


Figure 5

2.2 Hydrogen circuit

In order to optimise their durability, the fuel cells are fed with 50% excess hydrogen. In this particular case the hydrogen exceeding the reaction stoichiometry is vented but, in case of multi MW plant size, a recycling system that recovers the excess flow will be provided.

A safety valve releases the hydrogen into the stack if the pressure goes too high. The heated hydrogen is then cooled and humidified by directly injecting demineralised water, and is finally fed into the FORZA system.

2.3 Air/Water circuit

The oxygen required for the fuel cell to work is contained in the air. The air is supplied by a compressor and is fed directly into the FORZA system.

Along with the air the fuel cells are fed with the demineralised water required to humidify the air and to remove the heat produced inside the cells.

A flow of saturated air and liquid water goes out from the FORZA stacks. The excess air leaving the cells is separated from water and is cooled in a condenser to recover the residual humidity. Once the air has been cooled, it is released into the atmosphere. The demineralised water collected in a circulation tank is cooled and pumped to the fuel cells. Eventually, the excess of demineralised water is ready available at the outlet from the battery for plant use.

2.4 Electrical system

The current produced by the fuel cells is sent back to the electrolysis plant. Therefore, in order to allow the FORZA plant to work under various sodium chlorate plant load conditions, a DC/DC regulating system is fitted.

From the electrical point of view the connection between the DC/DC regulator and the rectifier that feeds the cell room is in parallel. The FORZA plant can therefore be disconnected from the system by proper switches for maintenance purposes, since it is electrically independent. This operation does not interfere with sodium chlorate production.

2.5 Power production

Figure 6 and 7 show the energy produced by the plant during the testing period: in particular, Fig.6 shows the daily energy production diagram during plant commissioning in June 2006, whilst Fig.7 shows the total amount of energy produced in 24/7 unattended mode during the period September – December 2006.

Figure 6: Operation parameters of the plant on June 21st, 2006

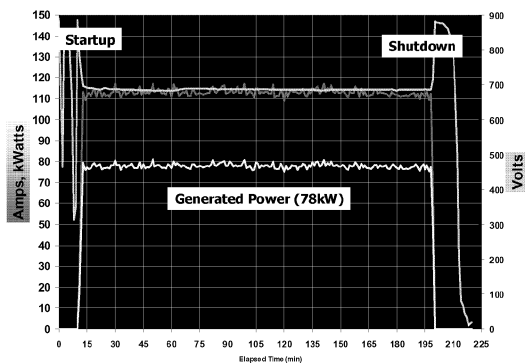
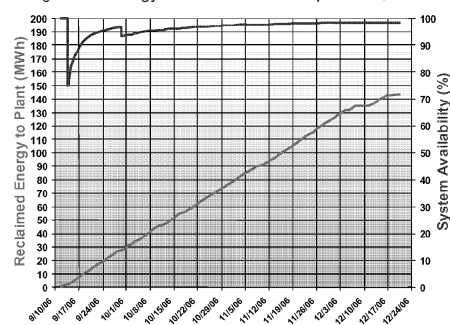


Figure 7: Energy cumulated from September, 2006

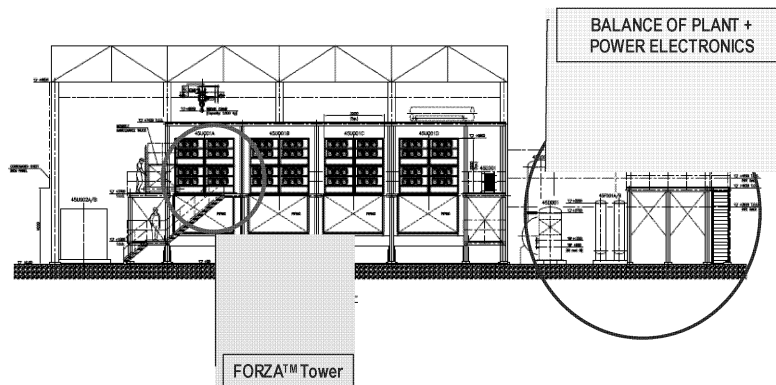


3 Sizing of multi-MW plants: a 2MW FORZA™ plant showcase

Nuvera and Uhdenora are collaborating for the development and construction of the 0.5 MW FORZA™ Tower: the tower will be the smallest modular part for the designing of multi-MW size plants.

In particular, as a showcase, Figure 8 shows the preliminary layout of a 2 MW size plant: the plant is made of 4 FORZA™ Towers and the related Balance of the Plant.

Figure 8: Showcase - 2.0 MW plant layout



3.1 Operating conditions of a 2 MW FORZA™ plant

Like all electrochemical devices, fuel cells are also subjected to performance reduction over time, which normally results in a reduction in the cell voltage for the same current and operating conditions.

Based on these considerations, the operating conditions for the “FORZA towers” were calculated for a nominal power (500 kW) that remains constant over time: this means that, as the plant keeps on operating, the current supplied to the cell increases gradually, thus resulting in hydrogen consumption increase.

Therefore in order to size the plant correctly, it is necessary to take the hydrogen consumption at then end of the fuel cells life, and to make sure that the hydrogen available from the C/A plant will meet the amount required at the end of this lifetime.

The quantity of hydrogen required can therefore be calculated as follows:

- ❑ The flow of hydrogen per tower is 57 kg/h (equivalent to 638 Nm³/h).
- ❑ For the four towers the hydrogen flow rate is 1812 Nm³/h.
- ❑ The maximum amount of hydrogen effectively consumed in the hydrogen-oxygen combining reaction is 426 Nm³/h.
- ❑ The maximum amount of H₂ required for the electrochemical reaction for the four towers for 24 hours a day, 355 days per year is 14,518,000 Nm³/year.

To supply about 14,5 million Nm³/year hydrogen the chlor-alkali plant must have a production capacity of about 48 kton chlorine (equal to 55 kton caustic soda) per year.

Acknowledgements

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