PROCEEDINGS OF ECOS 2023 - THE 36TH INTERNATIONAL CONFERENCE ON
EFFICIENCY, **C**OST, **O**PTIMIZATION, **S**IMULATION AND ENVIRONMENTAL IMPACT OF ENERGY SYSTEMS
25-30 JUNE 2023, LAS PALMAS DE GRAN CANARIA, SPAIN

Analysis of Sodium Water Reaction as heat source for district heating and cooling

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Abstract:

Finding new alternatives to current energy systems is a need to develop disruptive solutions. In this case, a complete new approach the Sodium as energy resource is described. Tradicionally, Sodium has been considered a risky element even if it were proposed as coolant in many applications, as nuclear or solar thermal plants. Such applications has been concerned by the explosive reaction of alkali as Na with water. In this communication, we analysed the altenative of profiting of such highly exothermic reaction for an energy use. Previuosly , we analised the utilization of sodium as propellant, and next steps presented in this paper shows the proposal of a sodium-water based heater to feed heating and cooling networks. A tentative configuration for the design of such heater, and the heat exchangers to adapt heated water temperatures will be presented. We present the conceptual design of a 13.5 MW district heating plant for a $\Delta T = 10^oC$ heating water from 60 to 70 ^{o}C, consuming 1 kg/s Sodium, reaching an efficiency of 95%, comparable with existing boilers..

Keywords:

Sodium-Water reaction, District Heating

1. Introduction

The energy sector is facing the need of a systemic transformation to reduce as much as possible the carbon dioxide content in the atmosphere, increasing the circularity of all the energy and industrial processes , as well as fulfilling the global energy demand. Current tendencies to improve the sustainaiblity of the energy system into the framework of the energy transition are based on the massive deployment of renewable primary energy sorces, the implementation of high capacity storage systems to manage intermitent generation of such sources. In addition, some authors consider nuclear energy [1] to support that high penetration of renewables to achieve zero-emissions targets. Additionally, even if fossil resources are expected to be axhausted at any time in the future, they would be able to contribute to decarbonise the energy system during such energy transition by the utilization of carbon captire and sequestration (CCS) technologies [2], as well as hydrocarbon pyrolysis [3].

Solutions for a decarbonised energy transition my be provided for electric and themal energy uses, either for industry or for heating/cooling application. Current solutions based on batteries, hydrogen or incremental developments of emerging, existing technologies, may have some limitations to provide a suitable scheme that would allow to comply with the maximun environmental targets. This could be specially critical for a complex system as it is the energy system itself, that should increase significatively its integration into circular processes coupling with other sectors. To increase the chance to achieve the required environmental targets seems necessay to analyze disruptive alternatives that can be added to the options that are currently available to increase the technological options to implement a sustainable energy system. Oxygen oxidation has generally been used as the fundamental form of enthalpy or chemical energy release, giving rise to combustion reactions. Another option is the use of water as an oxidizing element. One of the possibilities is the use of the sodium-water reaction, which responds to the exothermic balance expressed in 1:

$$Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2 \qquad \Delta H_0 = -141\frac{kJ}{mol_{Na}} = -6.13\frac{MJ}{kg_{Na}} \tag{1}$$

This reaction, when it occurs in excess of water, is followed by the dissolution of sodium hydroxide in water, which is also exothermic, and can offer, in the case of developing the reaction in a closed vessel, a practical heat generation of the order of 188 $kJ/mol_{Na}(8.174MJ/kg_{Na})$, The hydrogen produced recombines with oxygen that may be present in the reaction environment with an extra heat production, so that the total energy release

https://doi.org/10.52202/069564-0217

obtained in a total oxidation of Na to NaOH with water and oxygen and a subsequent dissolution of NaOH in water reaches 326.6 kJ/mol_{Na}($14.21 MJ/kg_{Na}$). In the case of developing an application that takes advantage of this energy, the final product would be a solution of solid hydroxide in water, which can be extracted in liquid form and continuously.

We have previously evaluated experimentally the sodium-water reaction in excess of water [5], qualifying its performance of sodium as candidate fuel for rocket propellant. Such works was one of the fist attempt to convert the inhetent risk associated to the use of sodium as coolant due to its high reactivity with water [6], to a potential valid decarbonised fuel. In this communication we analyse the application of such reaction to one of the most important sectors for the decarbonization of our Society. The residential sector accounts for a significant amount of CO_2 emissions due to the utilization of fossil fuels for climatization and heated water demand.

2. Sodium water reaction closed fuel cycle

The utilization of sodium as main fuel, combined with and oxydising agent as water, has as one of its primary source the common salt (NaCl). The extraction of sodium from sodium chloride, energy is needed according with the following electrochemical potential:

$$Na^{+} + Cl^{-} \longrightarrow Na + \frac{1}{2}Cl_2 \qquad E_0 = -4,07V \tag{2}$$

The energy that is needed, for instance, in form of electricity may be calculated by electrolytic conversion with the following semi-reactions:

$$Cathode : Na^{+} + e^{-} \longrightarrow Na \qquad E_0 = -2,71V \tag{3}$$

$$Anode : 2Cl^{-} \longrightarrow Cl_2 + 2e^{-} \qquad E_0 = -1.36V \tag{4}$$

The reaction enthalpy may be evaluated fromn the Gibbs energy of the reaction, which is calculated from the Faraday constant (F=96485 C/mol), and taking into account that one electron is needed for the formation of one Na molecule (23 g/mol) as:

$$\triangle G_0 = -n_e F E_0 = -96485 \cdot 4.07 \frac{J}{mol_{Na}} = 392.6 \frac{kJ}{mol_{Na}} = 17 \frac{MJ}{kg_{Na}} \tag{5}$$

The total enthalpy or enegy requirements for the dissociation of sodium clodride has to add the energy to heat it up to the fusion temperature and meld the compound, according to:

$$\triangle H = \triangle G_0 + C_{p,NaCl} \cdot (T_{f,NaCl} - T_a) + h_{fg,NaCl} = 17 + 1.9 + 0.32 \frac{MJ}{kg_{Na}} \approx 19.2 \frac{MJ}{kg_{Na}} \tag{6}$$

This number may be compared with the total amount of energy that is produced by the sodium water reaction (equation 1), what gives an overall potencial energy efficiency of the conversion of primary energy into heat of 73 % in the case of extracting Na from sodium chloride. Obviously, this figure is the maximum thermodynamic efficiency, that will be reduced by the losses of the electrochemical arrangement for Na synthesis, as well as the heat efficiency of the sodium-water reactor.

The utilization os NaCl as input raw material for the generation of the sodium reactant may be replaced by the recovery of sodium from the sodium hidroxide product of the raction. In this case, the redox reactions are:

$$Na^{+} + OH^{-} \longrightarrow Na + \frac{1}{2}H_2O + \frac{1}{4}O_2 \qquad E_0 = -3,11V \tag{7}$$

In this case, the amount of electrons (n_e) involves in the redox semireaction is 4, leading to a minimum potential energy demand of 8.2 MJ/kg_{NaOH}, that is a net energy demand for the recovery of sodium of 14 MJ/kg_{Na}. The efficiency of the NaOH/Na cycling depends only on its irreversibilities and the efficiency of the electrochemical and heat management equipment.

The energy needed to run both sodium synthesis processes is intended to be provided by low-carbon electricity, as wind, solar FV or nuclear.

https://doi.org/10.52202/069564-0217

3. Sustainability of the Sodium Water Reaction

One of the most important aspects related to the utilization of any energy source is the evaliation of its sustainability, what includes concepts as environmental impact, resources availability and circularity. The evaluation of the alternative of the sodium-water reaction, as a possible alternative to combustion in the context of the decarbonization of the energy system, can be analyzed based on sustainability criteria, and the comprison with the use of fossil resources today and some other alternatives. Among these generic characteristics for the evaluation of an energy source are:

- Greenhouse gases emissions related to its use as energy source.
- Circularity potential.
- Abundance and availability of primary resources.
- Energy density.

3.1. Environmental impact and circularity

The decarbonization of the energy system requires the development and implementation use of technologies with zero or very low emissions of greenhouse gases, such as methane or carbon dioxide, and to a lesser extent, water vapor or other triatomic molecules. As described, the sodium-water reaction has as its final product sodium hydroxide (NaOH) dissolved in water. Being a set of reactions that are not related to carbon chemistry, there is no recombination with oxygen to form CO or CO_2. It can be said that it is a high exergy thermal power generation without greenhouse gas emissions, which is compatible with applications in which fossil fuels such as natural gas are difficult to replace.

Regarding the potential for circularization, the result of the reaction is a solution of Na(OH) with water, which can be reintroduced into the reactor, increasing the hydroxide concentration. From a certain concentration after some recirculation cycles, after making the last thermal exchange, if it is allowed to cool in a open deposit, the NaOH crystallizes and precipitates [9]. The maximun concentration that may be reached depends on the process temperature, as seen in the NaOH/water system shown in figure 1. For instance, if operating at 25 ºC, NaOH concentration should not exceed 50 %.

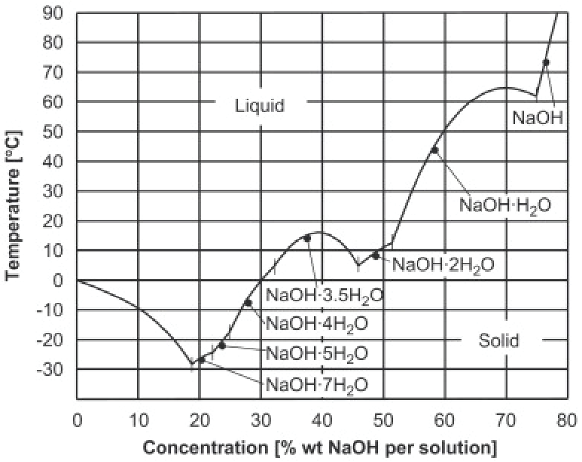

Figure 1: The NaOH–H2O system. Stability ranges of the different hydrates and the respective solidification lines [11]

3.2. Abundance of the primary source

Sodium is the sicth element in abundance accounting for 2.83 % of the Earth's crust [7]. That means that is far from being considered a risk from the geo-political point of view, being widely available. A list of the most abundant elements are listed in table 1. Sodiun is very reactive and it is not found as a single element. The most common sodium compound is sodium chloride. This very soluble salt has been leached into the oceans over the lifetime of the planet. Salt beds can be found where ancient seas have evaporated. It is also found in many minerals including cryolite, zeolite and sodalite.

The high availability of sodium compounds implies to fulfill one of the most important constraints for the sustainability of energy sources, that is the possibility to grant access to the resource to everyone.

Table 1: Element abundance on Earth [8]

Element	atomic number	% by weight
oxigen	8	46.60
silicon	14	27.72
aluminium	13	8.12
iron	25	5.00
calcium	20	3.63
sodium	11	2.83

3.3. Energy density

The development and application of the sodium water reaction convert sodium in an enegy vector, thjat could be compared with the rest of the vectors and storage techonology available. Suche comparison may be done in terms of energy density. The energy density of sodium has been evaluated as 14.2 MJ/kg_{Na} by mass or 13.8 GJ/m_3 by volumem in the case of adding the heat of the sodium-water reaction and the hydrogen oxidation, what is expected in excess of water. A comparison with other energy carriers is depicted in the table 2. All of the energy carriers that are considered now are based on liquid or gaseous substances. Sodium is a solid substance, what reduces energy lost during storage, enabling its use for long term storage.

From the point of view of the energy density, sodium is comparable in terms of volumetric capacity with other carriers as compressed natural gas, ammonia and liquid hydrogen. In any case, either compressed natural gas or different forms of hydrogen storage alternatives requires the implementation of criogenics or dedicated compression systems. Its performance is lower respect to liquid fuels, specially interms of energy per mass. Sodium as solid energy carrier is comparable with ammonia.

From this comparison, it can be assessed that sodium has energetic properties that are comparable with other energy vectors that are proposed as key for the implementation of a decarbonised energy system.

Table 2: Energy density of several energy carriers [10]

Carrier	Energy per mass (MJ/kg)	% Energy per volume (GJ/m^3)
Hydrogen (liquid)	143	10.1
Hydrogen compressed (700 bar)	143	5.6
Hydrogen at STP	143	0.0107
Natural gas (liquid)	53.6	22.2
Natural gas (250 bar)	53.6	9
Natural gas at STP	53.6	0.036
Methane at STP	55.6	0.0378
Gasoline	46.4	34.2
Diesel	45.4	34.6
Ammonia	18.6	11.5
Sodium	**14.2**	**13.8**

STP stands for Standard Temperature and Pressure (25 ºC, 1 bar)

4. Application to District Heating

I has been shown how the highly exothermic sodium-water reaction has certain potential to be integrated into the enegy system. Nevertheless, the reaction evolution should be controlled, as it has been done with combustion, to convert a reasonable reaction heat into a useful sevice. At this respect, district heating and cooling are one of the most important potential applications. Currently, the residential sector is the responsable of a very significant part of current CO_2 emissions in many countries, in many case above 50 % [4].

4.1. Process description

A full process that has been designed for the implementation of a district heating and cooling installation based on the sodium-water reaction is depicted in figure 2. The process is composed of the following functional circuits:

- Water feeding system (WFS).
- Sodium feeding system (SFS).

https://doi.org/10.52202/069564-0217

- Sodium-water reactor (SWR).
- Heat exchange to District Heating (HDH)
- Reactor outflow treatment system (ROTS).
- Air Purge System (APS).

The water feeding system (WFS) pumps water to the sodium water reactor. A pump controls the inflow of fresh running water to the process, that is mixed with pure water rejected by the osmotic separator of the reactor outflow treatment system (ROTS). The sodium feeding system (SFS) preheat sodium up to its liquid state (98 ºC) from the sodium inflow at room temperatura. It is composed by a preheater that melts sodium according to the inlet rate set up for the reactor. We have assumed in our design a sodium consumption of 1 kg/s as described in table 3. Such massflow is contolled by the reaction rate and volume of the sodium-water reactor (SWR). The basic parametes for the control of such reaction may be established by the experimental work already done for the characterization of the reaction in a fixed volume [5] and depicted in figure 3. Oor experimental work shows as the energy that is generated in the reactor is proportional to the amount of sodium that is present in the reaction chamber, with a low impact of the excess of water, or addicional material, as in this case is the remaining sodium hidroxide. As we intend to avoid water vaporization, the reactor should be pressurized.

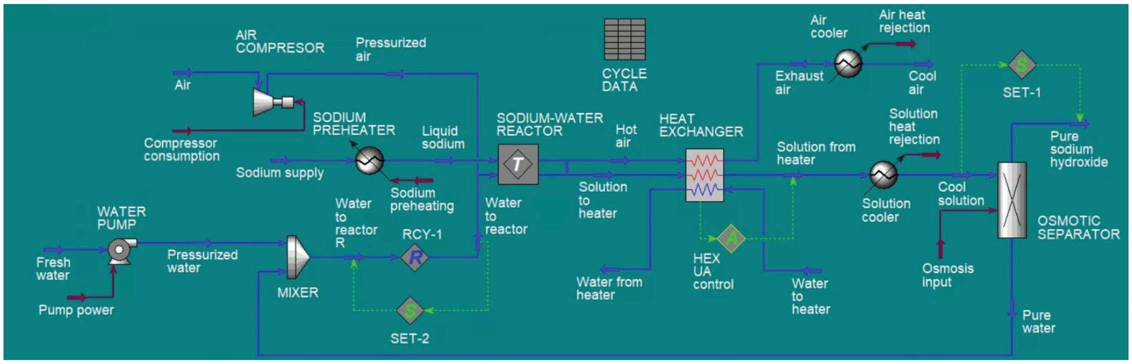

Figure 2: Process for the DHC application of the sodium-water reactor boiler including an osmotic separator for Na(OH)

The continuous reaction product stream passed to one leg of a heat exchanger of the HDH system to transfer the useful heat to the district heating loop. The service hear exchanger has an additional input from the air purge system (APS), which main purpose is to clean up the reactor stream from residual hydrogen that could remain in the reactor product stream. The air stream contributes to the total amount of heat transferred to the district loop, increasing efficiency.

The reactor outlet stream from the heat exchanger, composed by a sodium hydroxide solution in water is treated in the ROTS system to extract to extract pure Na (OH) and and water to be recirculated and mixed with running fresh water. The core of the reactor outflow treatment system is an osmotic separator that extract sodium hydroxide. Such separators are operating at low temperature [13] that is achieved by a cooler downstream the HDH. As an alternative, depending on the concentration of the solution, it can be solidified by lowering temperature. To improve the energy efficiency of the ROTS system, it i spossible to regenerate heat in the solution cooler exchanging energy between the pure water stream and the solution from the DHD. Such temperature reduction in the solution from water may happen with concentrations higher than 30 %. Such concentration may be achieved by the reduction of the pressure to enhance water vaporization of the mixture. For low concentration of Na(OH), the product stream can feed directly an electrolytis section to recover Na in case of the integration of a sodium recovery section. In that case, the facility will decouple electricity consumption from heat generation for the district heating, using sodium as storage.

4.2. Process data estimation

A conceptual analysis of the process that is proposed for the application of the sodium-water reaction to district heating (DH), that may be extended to dostrict cooling (DC) adapting the set-points of the control variables (mainly temperatures), has been modelled with UniSim R491 Suite [12]. From the previous discussion, we have analysed the substitution of the ROTS for a solution storage, that will increase the content of Na(OH) during operation. The simplified conceptuak process is depicted in fiigure 4 The size of the facility has been set to the processing of 1 kg/s of sodium, what is considered representative for a full scale district heating.

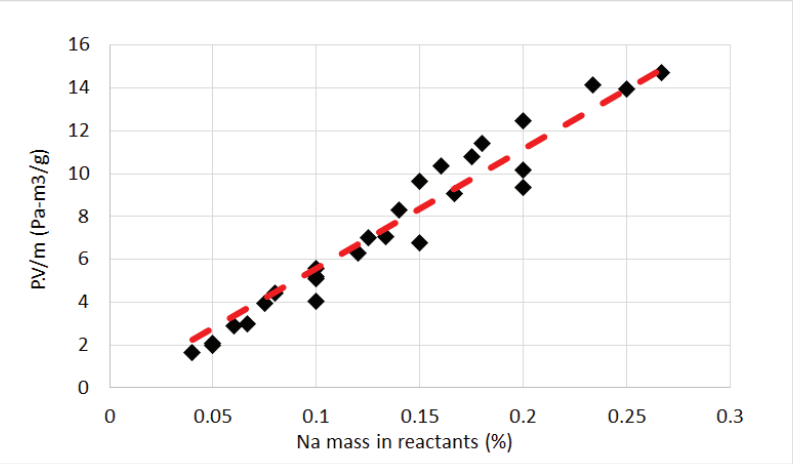

Figure 3: Normalised energy generation vs. Na in excess of water. [5]

Such sodium consumption corresponds to a heat plant of 13.5 MW. In this first analysys we have designed the service heat exchanger for district heating $\Delta T = 10^oC$ heating water from, 60 to 70 ^{o}C. In the case of the the application to district cooling, that may require higher temperatures, for instance, to drive absorption chillers, such service temperature may be upgraded by certain change in the set-points, as pressure and outlet temperature, of the reactor.

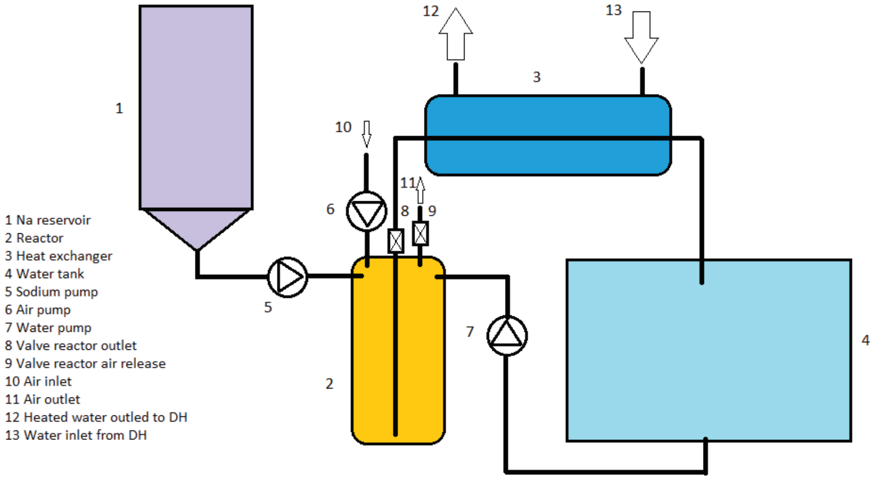

Figure 4: Conceptual design of a simplified process with Na(OH) solution recirculation

Pressure is one of the main parameters to avoid water vaporization from the reactor. The pressure into the reactor and the product and reactant loops will depend on the temperature that is intented to reach. In this case, we have fixed a pressure of 10 bar, providing a balanced between losses by water vaporization, compressor consumption and material requirements. For 10 bar, the outlet tempetature from the reactor has been set at 140 ºC, adjusting the reactants mass flow (water and sodium) to control the heat that is produced in the mixture. Water excess defined as the ratio of total water to the reactor respect to the stechiometric water of the reaction is 62. Water inyection allows the control of the temperature into the reactor preventing overheating.

The total efficiency of the facility is defined from the heat power to the district heating (Q_{DH}), the total heating value of the complete oxidation of sodium (including hydrogen combustion, HV_{tot}) and the auxiliary electric consumption (compressor, pumps,) (P_{aux}):

$$\eta = \frac{Q_{DH}}{HV_{tot} + P_{aux}} = \frac{14093kW}{14206kW + 551kW} = 0.95 \tag{8}$$

The mass balance of the facility is descibed in table 3, with the temperature and pressure of each main stream. The main process data for the facility are sumarised in table 4.

Table 3: Main process mass balance datasheet

Stream	massflow (kg/s)	T (^oC)	P (bar)
Fresh water	0,8	15	1
Pure water from ROTS	50.1	80	10
Aire	1. 513	15	1
Water to reactor	50.9	78.92	10
Sodium supply	1	15	10
Liquid sodium	1	98	10
Solution to heater	51.9	140	10
Pure Na(OH)	1.75	80	10
Water to DH	335.1	70	1

Table 4: Main process energy balance datasheet

Equipment	Power (kW)	Specific consumption (Wh/kg$_{watertoDH}$)
Auxiliaries	550.3	0.047
Water pump	0.95	$8.2 \cdot 10^{-4}$
Heaters	6035	0.52
Heat power to DH (Q_{DH})	13540	-
Thermal losses APS	245.3	0.02

5. Conclusions

There is a need for disrupting technologies that could deiversify the available tools to tackle the enormeous challenge of the global climatic crisis. There is a general consensus about the need to shift from a fossil-based society to a more sustainable system that could be more integrated into the natural mass and energy balance of the Earth, reducing as much as possible the impact of the current human activity. That transformation should find alternatives to carry out succesfully such deep systemic changes. Some technologies are on the table. In paricular renewable based primary sources as wind and solar are having every year a more important role. Nevertheless, additional technologies are needed to complement and be added to those sources to solve some of theur limitations as management capacity, inttermitency and storage.

The utilization of sodium as energy vector has been scarcely developed. In this communication we have described how sodium may be considered as an energy vector, with storage capacity and potential of application to end users. In this case, we introduce a district heating (that may be extended to cooling) facility that provides heated water with a reasonable efficiency (95 %), comparable with existing boilers, with storage capacity if a sodium electrolytic section is added. In that case, a circular operation Na-Na(OH) will have a potential efficiency very similar with other Power-to-Heat or Power-to-Power storage technologies, as thermal storage, Carnot batteries [15] and better than electrolitic hydrogen (electrolyser-fuel cell combination, Power-to-Heat) [14]. Heat pumps offers as well a good solution to impove efficiency of district heating solutions depending on the ΔT that they should provide, with Coefficients of Performance (COP) between 3 and 5, but must add as well Power-to-Power energy storage to integrate energy management cost.

The description of the facility includes a definition of the process with its functional blocks, as well as the mass and energy balance, to process 1 kg/s of sodium, estimating the water excess that should be needed to keep the temperature and pressure conditions to reasonable thermal losses and auxiliary energy consumption.

Further work will apply a complete parametric analysys of the facility design to optimize efficiency and describe more in detail the facility to operate to use surplus renewable electricity production for heating delivery, adding management and storage capacity to decarbonised electric grid, and coupling electric and thermal networks. A lot of work should be done to evaluate the application of this technology to low/medium temperature applications as district heating, as well as high temperature application including thermal conversion to power.

https://doi.org/10.52202/069564-0217

Acknowledgments

This work does not received any funding, but it has been developed thanks to the effort of staff involved in the PhD program of sustainable energy, nuclear and renewable of the UPM, for the PhD thesis of Juan Guerrero Padrón.

Nomenclature

n_e: Electrons involved in the redox reaction.
E_0: Standard electrochemical potential (V)
G_0: Gibbs energy in standard conditions (MJ/kg)
$h_{fg,NaCl}$: Latent heat of NaCl
Q_{DH}: Heat power to the district heating (kW)
HV_{SWR}: Heating value of the reaction (kW)
Q_{aux}: Auxiliary heating power in the process (kW)
P_{aux}: Electric power consumption in the process. (kW)
WFS: Water feed system
SFS: Sodium feed system
SWR: Sodium-water reactor
HDH: Heat exchange to District Heating System
ROTS: Reactor outflow treatment system
APS: Air Purge System

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