POLITECNICO DI MILANO

Scuola di Ingegneria Industriale e dell'Informazione

Corso di Laurea Magistrale in

Ingegneria Nucleare

Load Following with Nuclear Power by off-peak Hydrogen Production

Relatore: Prof.Ing. Marco Ricotti

Correlatore: Dr. Giorgio Locatelli

Tesi di Laurea di:

Andrea Fiordaliso

801454

Anno Accademico 2014-2015

Index

List of Figures

List of Tables

ABSTRACT, ENGLISH:

Nuclear power has been historically considered a base-load technology. Nowadays the increasing penetration of intermittent and must-run power sources (i.e. PV, wind) in the electric grid is forcing Nuclear Plants (NPP) to operate in Load Following mode, reducing the output power during the off-peak hours by mean of the insertion of negative reactivity in the core. This operation is very inefficient since NPP costs are mainly fixed and sunk. A more efficient alternative is to maintain the primary loop at full power, and use the not required (by the grid) power to obtain valuable products by an auxiliary plant.

Starting by this approach, this thesis assesses the techno-economic feasibility of the coupling between a NPP and five technologies: plastic pyrolysis, wood pelletisation, water electrolysis (WE), high temperature steam electrolysis (HTSE), sulfur-iodine cycle (SI). The first two are abandoned because of technical reasons. The economic analysis shows that in the medium term hydrogen from WE (electric application) can be produced at relatively low prices within certain electricity price contexts. The last two technologies (and in particular the SI cycle which a completely thermal application) despite being still under R&D, proved to be very attractive in a long term perspective for their capability to produce hydrogen with high efficiency; but only if the technology achieves a certain level of development.

ABSTRACT, ITALIAN :

Il nucleare è sempre stato considerato una tecnologia adatta a servire il carico di base. Oggi la crescente penetrazione di impianti di potenza intermittente e *must-run* nella rete elettrica (cioè fotovoltaico ed eolico) sta costringendo gli Impianti Nucleari (NPP) ad inseguire il carico elettrico (*Load Following*), riducendo la potenza generata durante le ore di bassa richiesta per mezzo di una inserzione di reattività negativa nel nocciolo. Questa operazione è molto inefficiente, dato che i costi del nucleare sono principalmente quelli fissi e i sommersi. Una alternativa più efficiente consiste nel mantenere il circuito primario a potenza nominale, e usare la potenza non richiesta (dalla rete) per ottenere prodotti attraverso un impianto ausiliario.

Partendo da questo approccio, questa tesi valuta la fattibilità tecnico-economica di un accoppiamento tra un NP e cinque diverse tecnologie: pirolisi della plastica, pellettizzazione del legno, elettrolisi dell'acqua (WE), elettrolisi di vapore ad alta temperatura (HTSE), ciclo Zolfo-Iodio (SI). Le prime due sono scartate per ragioni tecniche. L'analisi economica dimostra che sul medio termine si può produrre idrogeno con WE (applicazione elettrica) a prezzi relativamente bassi in certi contesti di costo dell'elettricità. Le ultime due tecnologie (e in particolare la SI, che è un'applicazione completamente termica), sebbene siano ancora entrambe in una fase di Ricerca e Sviluppo, si dimostrano interessanti sul lungo periodo per la loro capacità di produrre idrogeno ad alta efficienza; ma solo se la tecnologia raggiungerà un sufficiente livello di sviluppo.

Estratto in Italiano:

Nel primo decennio del XXI secolo si è assistito ad un 'rinascimento nucleare', che, dopo un rallentamento subito a seguito dell’incidente di Fukushima, ora sembra ripartire [1], [2].
In questi anni la popolazione mondiale sta crescendo rapidamente, portando ad un aumento della domanda di energia: l'Agenzia internazionale dell'energia (AIE) prevede che la domanda globale di elettricità aumenterà del 2,2 per cento all'anno fino al 2035 [3].
Inoltre, la crescente sensibilità alle tematiche ambientali che si sta diffondendo globalmente in questi anni [4], [5], incoraggia norme sempre più vincolanti sulle emissioni di gas nocivi.
In questo contesto un potenziamento della tecnologia nucleare, al fianco di quelle rinnovabili, può consentire la prospettiva di sviluppo sostenibile sul lungo periodo, limitando le emissioni di gas serra.
La decisione di seguire questa direzione o meno in futuro spetterà ai politici dei paesi più sviluppati e in via di sviluppo. In ogni caso, l'energia nucleare supporta già adesso una quota rilevante della produzione totale di energia elettrica, con più di 2.410 TWh prodotti nel 2014 [6]; e considerando il gran numero (contando sia gli impianti operativi che in costruzione) di centrali nucleari in tutto il mondo [7], continuerà a svolgere un ruolo essenziale anche per i prossimi decenni, come minimo.

Inoltre, il portfolio energetico in diversi paesi sviluppati e in via di sviluppo sta costringendo le centrali nucleari ad operare inseguendo il carico (Load Following), e quindi lavorare a potenza variabile [8].
Di conseguenza, i progettisti e proprietari dei reattori nucleari hanno studiato (e potenziato) le capacità degli impianti di lavorare in modalità Load Following [8], riducendo la potenza, e quindi l'energia elettrica complessiva prodotta durante la vita dell'impianto nucleare.

Poiché una caratteristica specifica dell'energia nucleare è l'elevata incidenza del costo d’impianto (60%, contro, ad esempio il 15% per un turbogas, [9]), una riduzione della produzione rappresenta una perdita di ricavo senza comportare una significativa riduzione dei costi per il risparmio di combustibile.
In altre parole, il Load Following con il nucleare è una sottoutilizzazione dell’impianto. Questa tendenza esorta la comunità scientifica a cercare sempre nuove soluzioni tecnologiche, per sfruttare pienamente il potenziale di un reattore nucleare.
Storicamente, le centrali nucleari (NPPs) sono state utilizzate principalmente per coprire il carico di base della domanda di elettricità [8].
Questa è la modalità più economica e tecnicamente più semplice di funzionamento: variazioni di potenza sono limitate a regolazione di frequenza per fini di stabilità della rete, e spegnimenti per motivi di sicurezza.

Ancora oggi, la maggior parte delle centrali nucleari sono utilizzate per il carico di base, e funzionano a un livello di potenza fisso [10], ma vi è un numero crescente di paesi (ad esempio Francia e Germania) nei quali la situazione è cambiata, e le centrali nucleari sono costrette a lavorare in modalità Load Following [8]. Ad esempio, in Francia il contributo del nucleare nel portfolio elettrico nazionale è così rilevante (75% [8]) che non è possibile lasciar funzionare a pieno carico tutte le centrali durante la notte.

Anche se la Francia è un'eccezione per quanto riguarda il contributo della produzione di energia nucleare, diversi paesi che presentano contributi al di sopra del 50%, segnatamente il Belgio, l'Ungheria, la Slovacchia e l'Ucraina [6], potrebbero riscontrare lo stesso problema.

C'è un altro motivo principale per cui gli Impianti Nucleari possono essere costretti a seguire il carico: ciò si verifica quando nello stesso paese (e quindi sulla stessa rete elettrica) una parte sempre crescente del portfolio di potenza installata è costituito da fonti di potenza intermittente e non controllabili, come fotovoltaico ed eolico, come accade ad esempio in Germania [8].

Dal momento che questi impianti non sono controllabili (funzionano solo quando sole e vento sono presenti), poiché l'offerta di potenza sulla rete elettrica non può superare la domanda, altri impianti devono ridurre la propria potenza di output.

In ogni caso, l'output di potenza di uno specifico NPP è fortemente dipendente dal portfolio energetico e dalle caratteristiche della domanda specifici dell'area geografica in cui quest'ultimo è collocato.

Chiarito dunque che ogni centrale che segue il carico ha una propria specificità, si può dire che gli impianti nucleari che operano in Load Following si muovono normalmente entro determinati parametri:

- la potenza di output varia normalmente tra il 50 e il 100% della potenza nominale;
- il carico è tendenzialmente vicino al 50% nelle ore notturne, e al 100% nelle ore diurne.

Questa situazione costringe gli operatori ad implementare o migliorare le manovrabilità delle loro centrali nucleari, per essere in grado di variare periodicamente (su base giornaliera e stagionale) la fornitura di energia elettrica in funzione di variazioni della richiesta di potenza, come spiegato da [8].

Centrali nucleari moderne, come i PWR operanti in Francia, sono progettate per avere un'ottima manovrabilità [11]. Diverse centrali nucleari francesi seguono un programma di carico variabile, con una o due grandi variazioni di potenza al giorno [8]. Ci sono vari metodi per far decrescere la potenza generata da un reattore nucleare [9], ognuno dei quali prevede l'inserzione di reattività negativa nel nocciolo, comportando un abbassamento della potenza termica generata e un transitorio termodinamico, che sottopone a stress termomeccanici i componenti del reattore. Anche se questo problema può essere mitigato, il Load Following resta essenzialmente un sottoutilizzo dell'impianto. Diversamente da quanto avviene per le centrali a gas, nel nucleare non si ha un risparmio significativo nel ridurre la produzione di energia elettrica, in quanto [9]:

- il costo d'impianto, ossia quello principale, è un costo sommerso;
- i costi di O&M (ad esempio il personale) sono fissi e indipendenti dal tasso di produzione;
- i costi del combustibile nucleare rappresentano solo il 10% -15% dei costi complessivi.

Pertanto, le conseguenze economiche della riduzione di produzione sono principalmente legate al fattore di carico, che provoca indirettamente un aumento del rapporto costo d’impianto / energia prodotta. Dunque effettuare Load Following inserendo reattività negativa nel nocciolo risulta essere un grande spreco di risorse.

Il campo di ricerca in cui si muove questa tesi si basa su un'idea chiave: poiché il Load Following per le centrali nucleari non è evitabile, si può trovare un modo per eseguirlo senza sprecare risorse.
L'idea di base del 'Load Following by an Auxiliary Plant’ è di unire i due concetti di Load Following e cogenerazione in un'unica strategia operativa: il reattore nucleare funziona sempre alla potenza nominale, lasciando immutato il circuito primario. Durante le ore di carico elevato (giorno) la centrale nucleare fornisce il massimo di potenza elettrica alla rete, mentre durante le ore di bassa domanda (notte) l'elettricità non richiesta (o il calore di processo) è diretta a un impianto industriale, che produce un determinato bene. L'accoppiamento si dimostra particolarmente virtuoso per gli impianti industriali che richiedono una grande quantità di energia termica o elettrica, e il cui costo di produzione principale è rappresentato dall’approvvigionamento di questi ultimi.

Tra i possibili impianti ausiliari, le applicazioni non-elettriche richiedenti calore a bassa temperatura sono le preferibili, in quanto in questo modo il calore viene fornito all’impianto prima di essere convertito mediante una conversione elettrica non efficiente [12]. Studi precedenti [12], [13] hanno dimostrato che, rispetto ad un accoppiamento con una applicazione termica, i reattori nucleari di taglia medio-piccola (SMR) sono più adatti rispetto a quelli di taglia grande (LR), in quanto riducono l’inefficienza complessiva comportata dal fatto che il reattore lavora lontano dalle condizioni nominali.

Le possibili applicazioni candidate all’accoppiamento con un NPP devono rispettare una serie di criteri.
L'accoppiamento con un'applicazione elettrica è il più semplice, per diversi motivi:

- non richiede alcuna modifica nel design del NPP, in quanto l’output della centrale rimane esattamente lo stesso (potenza elettrica nominale) che stia lavorando per la rete, o per l’impianto ausiliario.
- per la stessa ragione, nessuna modifica del ciclo TD è coinvolta. Ciò significa che i due flussi di energia (quello destinato alla rete, e quello all’impianto ausiliario) sono separati all’esterno del NPP;
- non è richiesta prossimità tra l'impianto ausiliario e il NPP, dal momento che l'energia elettrica può percorrere lunghe distanze con perdite relativamente piccole.

Essenzialmente qualunque impianto che richiede elettricità può essere accoppiato con una centrale nucleare; la questione è che:

- la sua richiesta di potenza deve essere molto grande;
- deve essere sufficientemente flessibile da poter funzionare a piena potenza durante la notte, e rimanere spento durante il giorno.

Possibili applicazioni non elettriche hanno bisogno di un trattamento più approfondito.
Un impianto ausiliario per essere compatibile con la gestione di un NPP in modalità Load Following, dovrebbe:

- richiedere una grande potenza termica (circa 2.000 MWth, o una combinazione equivalente di potenza elettrica e termica);
- richiedere calore relativamente a bassa temperatura, cioè sotto i 300 °C per l'accoppiamento con un PWR [9] ;
- non avere un'elevata inerzia termica;
- prestarsi a variazioni di carico giornaliere, con una dinamica piuttosto veloce.

La possibilità di effettuare cogenerazione e load following con diverse possibili applicazioni è già stata oggetto di uno studio di fattibilità, tecnica ed economica. I risultati più rilevanti presenti in letteratura sono riassunti nella tabella seguente.

	Fattibilità Tecnica	**Fattibilità Economica**	**Riferimento bibliografico**
1.Desalinizzazione dell'acqua	Sì	Sì	[14]–[16],[17], [18]
2. Raffinazione del petrolio	Sì	No	[19]
3. Estrazione di scisto bitumoso	Sì, ma possible necessità di NPP mobili	Oggetto di studio	[20]–[22]
4. Biocombustibile (da alghe)	Sì la cogenerazione No Load Following	Non studiata	[12], [13]
5. District heating	Sì	Sì la cogenerazione Load Following inaccettabile socialmente	[23]

I candidati impianti industriali che sono stati considerati nel presente lavoro di tesi sono:

- Un reattore di pirolisi dei rifiuti in plastica, per la produzione di combustibili diesel-simili;
- Un impianto di produzione pellet, ottenuto da rifiuti di legno di trasformazione;
- Un impianto di produzione di idrogeno.

In una fase di analisi preliminare si cerca una risposta alle seguenti domande:

1. Qual è la dimensione tipica dell'impianto?

2. Sarebbe tecnicamente possibile costruire un impianto di 2.000 MWth equivalenti?
3. Ci sarebbe abbastanza materia prima perché questo ipotetico impianto possa essere accoppiato con un NPP?
4. Ci sarebbe abbastanza richiesta per sottoprodotto ottenuto?

Se la risposta alle ultime tre domande è sì (o almeno è incerta), allora è possibile procedere ad una ulteriore fase di analisi, e affrontare le problematiche del dimensionamento tecnico, e infine eseguire la valutazione economica. Altrimenti, la possibilità di eseguire Load Following con un NPP attraverso questo impianto si ferma qui.

Gli impianti nucleari presi come riferimento per l'accoppiamento sono: un LR PWR (1,340 MWe), un impianto costituito da 4 moduli di SMR PWR (335 MWe ognuno), e un impianto costituito da 4 SMR VHTGR (335 MWe ognuno). Tutti generano la stessa quantità di energia in un anno, e presentano una 'Energia in eccesso' (non richiesta dalla rete) pari a 1,859 GWh elettrici (5,548 termici, se il NPP è un PWR). Dunque il primo criterio di selezione per qualunque impianto candidato è la possibilità di raggiungere questa taglia.

La pirolisi della plastica è un processo di degradazione termica dei rifiuti in un ambiente privo di ossigeno [24].
In Europa circa 8,9 Mtonne/anno di plastica sono stati riutilizzati per il recupero di energia [25].
Oggigiorno quasi tutto il recupero di energia è realizzato mediante incenerimento, mentre la pirolisi plastica rappresenta una tecnologia di nicchia.
Comunque, supponendo che la pirolisi possa sostituire completamente l'incenerimento, e che sia tecnicamente fattibile portare la plastica raccolta in tutta Europa in un unico sito, dove questa venga sottoposta a pirolisi, si calcola il fabbisogno energetico di questo ipotetico impianto.
I gestori dei pochi impianti di pirolisi della plastica al mondo non forniscono i dati dei consumi energetici, tuttavia dopo una serie di contatti con accademici interessati ai trattamenti termici della plastica, è stato ottenuto il valore di energia specifica richiesto dal processo: 6 MJ/kg.
Attraverso un calcolo approssimato si dimostra che per sottoporre a pirolisi tutta la suddetta quantità di plastica sarebbero necessari circa 15 mila GWh termici, che sono forniti da meno di 3 NPPs. Considerando che è logisticamente impossibile far convogliare tutta la plastica d'Europa in un solo impianto, ma che al massimo si potrebbe considerare un impianto di pirolisi ogni qualche milione di abitanti (si consideri 1 per macroregione di 5 milioni di persone), si comprende come le quantità di plastica disponibili sarebbero totalmente incompatibili con la taglia dell'impianto nucleare. Dunque la plastica è da scartare.

I pellet sono combustibili ottenuti da materia organica compressa. Essi sono generalmente costituiti da segatura compattata e scarti industriali derivanti dalla macinazione di legname, e dalla fabbricazione di prodotti in legno e mobili.

In tutto il mondo c'è una grande produzione di pellet di legno: solo in Nord America 13 impianti, per una capacità totale di 2,9 Mtonne all'anno sono attualmente in costruzione [26]; aggiungendo questo dato agli impianti già operativi, si raggiunge una capacità totale di oltre 22 Mtonne/anno. La maggior parte di questi impianti hanno dimensioni comprese tra 10.000 e 400.000 tonnellate/anno [26]; la più grande è a Waycross, GA (di proprietà di RWE Innogy Cogen): 825.000 tonnellate/anno [26]. Per quanto riguarda i consumi di energia, anche in questo caso le società che gestiscono i grandi impianti non condividono i propri dati; tuttavia, una società italiana che opera in questo settore (Italiana Pellets), con un impianto di dimensioni medie (120.000 tonnellate/anno) ha fornito i propri dati tecnici. Questi, scalati su un impianto delle dimensioni di 1 Mtonne/anno consentono di calcolare in maniera approssimativa l'energia richiesta da quest'ultimo. Il ottenuto (1,558 GWh termici equivalenti) è ancora quasi 4 volte inferiore all'energia in eccesso dal NPP. Inoltre, questa taglia è considerata dagli operatori del settore come la massima ipotizzabile per un impianto di pellet, a causa di problemi logistici legati all'approvvigionamento della materia prima. Quest'ultima infatti non è legno direttamente proveniente dal disboscamento delle foreste (che essendo un bene prezioso viene utilizzato per la fabbricazione di mobili ed oggetti vari), ma è materiale di scarto delle falegnamerie industriali.

Dato che il valore aggiunto del processo in termini energetici è relativamente basso, il fattore chiave per la redditività economica della pellettizzazione è rappresentato dalla logistica di approvvigionamento del legname di scarto: i tecnici stimano che quest' ultimo può viaggiare per 30--40 km al massimo dalla raccolta alla trasformazione, altrimenti i costi di trasporto superano i possibili ricavi. Per questo motivo, questi impianti sono posti al centro di grandi distretti di lavorazione del legno, e la loro dimensione è limitata dalla quantità di materiale di scarto reperibile, più che da altre ragioni tecniche. A seguito di queste considerazioni anche l'impianto di pellettizzazione deve essere scartato.

Nei paesi industrializzati e in via di sviluppo, le emissioni dei veicoli a motore sono tra i principali motivi della scarsa qualità dell'aria urbana. Secondo [27], l'idrogeno è una delle migliori opzioni di combustibile pulito per ridurre le emissioni dovute ai veicoli a motore. In ogni caso, già oggi esiste una grande produzione di idrogeno in tutto il mondo: 50 milioni di tonnellate l'anno [18], che corrisponde grosso modo a 560 miliardi di Nm3.

Se l'intera quantità di idrogeno prodotto in un anno fosse ottenuto da elettrolisi dell'acqua, prendendo un input di energia di 48,2 MWh_el/Tonne_H2 , (l'origine dei valori utilizzati nella presente sezione sarà giustificata nelle seguenti sezioni: 2.2.4 e 3.3) di questa tesi; questo significa che sarebbe necessario 2,41 * 10^6 GWh di energia elettrica per la produzione di esso. Considerando un NPP di 1 GWe di taglia, che produce 8.322 GWh di energia elettrica per 1 anno, ci potrebbero essere 290 centrali nucleari nel mondo che producono energia elettrica 24 ore al giorno per fornire la richiesta di idrogeno. Se questi lavorassero in modalità Load Following, fornendo così soltanto la metà della propria potenza di output e solo durante la notte (8 ore al giorno, per esempio), questo numero potrebbe essere moltiplicato per circa 6: il che porta a 1.740 centrali nucleari da 1 GWe impegnati per la produzione dell'idrogeno. Se solo l'1% della produzione totale di idrogeno fosse dovuta a Load Following con l'energia nucleare, 17 centrali nucleari sarebbero necessarie. Questi semplici calcoli dimostrano che esiste una domanda di idrogeno sufficiente nel mondo per giustificare un impianto di produzione di H_2 di qualsiasi dimensione. Inoltre, poiché i processi che sono contemplati in questa tesi ottengono idrogeno dall'acqua, la potenziale materia prima può essere considerata infinita. Chiarito questo, è anche evidente che prima di costruire un impianto di idrogeno in un sito, è necessario porsi il problema dello smaltimento di tutta la produzione, ovvero:

- analizzare le esigenze dell'area industriale circostante l'impianto, se l'idrogeno dovesse essere venduto;
- altrimenti studiare il fabbisogno di idrogeno di un ulteriore impianto industriale (per quale l'H_2 sarebbe una materia prima), servito dall'impianto in esame.

Nel presente lavoro di tesi è stato condotto un ampio studio della letteratura scientifica riguardante la produzione dell'idrogeno da fonte fossile e non, dal quale si possono trarre le seguenti conclusioni:

- la produzione da fonte fossile (che comporta evidentemente rilevanti emissioni di CO_2 [28]) costituisce circa il 96% della produzione mondiale di H_2 [29];
- il restante 4% si effettua tramite l'elettrolisi dell'acqua (WE) [30];
- la altre tecnologie di produzione per separazione dell'acqua sono oggetto di ricerca e sviluppo, ma non sono disponibili su scala commerciale;
- il Reforming del Metano è la tecnologia attualmente più diffusa, nonché la più economica, e dati gli attuali prezzi di mercato del gas e dell'elettricità, senza l'applicazione di una carbon tax severa, è poco realistico che la WE possa competere con il Reforming del Metano [28];
- La WE è una tecnologia pienamente sviluppata e ampiamente applicata e studiata in combinazione con varie fonti di energia, ed in particolare con le rinnovabili [31]–[33]. Si tratta di una applicazione totalmente elettrica che richiede circa 4,5 kWh elettrici/Nm^3_H_2 prodotto. I costi di questo processo sono noti e sono stati reperiti combinando i valori disponibili in letteratura a quelli forniti direttamente dai produttori di elettrolizzatori (EZ);
- L' elettrolisi di vapore ad alta temperatura (HTSE) è un'applicazione principalmente elettrica (2.5 kWh elettrici/ Nm^3_H_2 [30]), ma richiede un significativo contributo termico per trasformare l'acqua di alimento in vapore a 850°C (temperatura operativa), ovvero circa 0,9 kWh termici/ Nm^3_H_2 [30]. I reattori elettrochimici di questo tipo (detti SOEC) esistono solo su scala del kW. Non essendo disponibili elettrolizzatori di vapore a livello commerciale, i costi di questa tecnologia, ed in particolare il costo d'impianto, sono estremamente difficili da prevedere;

- Tra tutti i cicli termochimici per la produzione di idrogeno proposti in letteratura, quello Zolfo-Iodio (SI) è tra i più promettenti e avanzati rispetto alla fase di ricerca [30]. Si tratta di una serie di reazioni chimiche (che avvengono in tre step) nelle quali tutti i reagenti vengono riciclati, ad eccezione di H_2O, che si scinde in H_2 ed O_2. Idrogeno e ossigeno, una volta prodotti, vengono estratti dal ciclo. Il consumo energetico del processo è ancora incerto, dato che lo stesso non viene ancora realizzato in maniera stabile e regolare [34]. Tuttavia esso può essere stimato in circa 6 kWh termici (risultato ottenuto a partire dai dati disponibili in [30], e calcolato nel paragrafo 3.6). Anche in questo caso, come per i SOEC, è molto difficile prevedere i costi che in futuro potrebbe avere questa tecnologia.

Per quanto riguarda la WE, vengono considerate quattro strategie operative:

- BC 8 (Base Case 8), che prevede Load Following con funzionamento degli EZs nelle 8 ore notturne;
- BC 12, che prevede Load Following con funzionamento degli EZs nelle 12 ore notturne;
- Short Term Operating Reserves (STOR);
- Fast Reserves (FR).

La descrizione del funzionamento degli EZs nelle ultime due strategie richiede una spiegazione più complessa di quanto possibile in questa trattazione sintetica, per la quale si rimanda ai paragafi 2.4.2, 3.3.2 e 4.2.5. Tuttavia in estrema sintesi si può dire che in queste modalità operative gli elettrolizzatori funzionano come riserve di elettricità per la rete elettrica. Una parte degli elettrolizzatori costituenti l'impianto di WE lavora a pieno carico anche di giorno. Nel caso di improvvisa richiesta di elettricità da parte della rete, i suddetti EZs vengono rapidamente spenti e la potenza che era destinata ad essi viene dirottata, appunto, sulla rete stessa. Questa modalità operativa consentirebbe ai reattori nucleari di accedere al mercato delle Riserve di elettricità, cosa finora impossibile. Tuttavia l'effettiva fattibilità tecnica di questa modalità operativa e il suo effetto sulle prestazioni degli elettrolizzatori sono attualmente imprevedibili; dunque diversi possibili scenari sono stati ipotizzati a questo proposito.

Si ipotizza che le altre due tecnologie di produzione dell'idrogeno (HTSE ed SI) lavorino secondo la modalità operativa BC 8, descritta precedentemente.

Le tre tecnologie che sono state brevemente presentate nel paragrafo precedente (WE, HTSE, SI) sono state oggetto di un'analisi tecnico-economica, nell'ipotesi di un loro accoppiamento con un impianto nucleare che operi secondo la strategia del Load Following.

I risultati principali dell'analisi tecnica sono i seguenti:

- La WE, essendo un'applicazione elettrica, è una tecnologia flessibile che può essere facilmente accoppiata con un NPP all'interno di una strategia di Load Following, ma gli EZs necessitano di essere tenuti in funzionamento a 20% del carico durante il giorno, al fine di evitare un aumento della velocità di degradazione;

• L'operazione STOR non presenta fattori evidenti di insostenibilità per l’EZ, quindi non si prevede una significativa diminuzione dell’efficienza rispetto all'operazione Base Case;
• D'altra parte l'operazione FR mette a dura prova l’EZ, che tuttavia è tecnicamente in grado di eseguire velocemente lo spegnimento (rendendo così disponibile l’elettricità per le riserve) e riaccendersi rapidamente. Questa operazione ragionevolmente causerà una rilevante accelerazione del degrado dell'efficienza;
• L’ HTSE, nonostante l'alta temperatura, è principalmente un'applicazione elettrica;
• L’ impianto HTSE può essere accoppiato in un design cogenerativo con un VHTGR, ma questi ultimi non sono chiaramente diffusi come i PWR. L'accoppiamento con un PWR (che fornisce calore a circa 290 °C [35]) è possibile prevedendo un ulteriore surriscaldamento del vapore ad opera di uno scambiatore di calore che brucia gas. Questa soluzione è interessante dal punto di vista energetico, perché il surriscaldatore a gas dovrebbe fornire solo 72 MWth, ad un HTSE che prevede 618 MWe di input. In ogni caso la sua fattibilità tecnica deve essere dimostrata;
• Eseguire Load Following con un HTSE è più difficile, perché non è chiaro se un impianto che opera a 850 °C possa facilmente adattarsi a cambiamenti periodici della potenza in ingresso. Tuttavia la fattibilità di tale accoppiamento non si può escludere a priori. Inoltre la natura modulare dell’ impianto HTSE (fatto da centinaia di SOECs) potrebbe essere un fattore favorevole;
• L’impianto SI può sicuramente essere accoppiato con un VHTGR in un design cogenerativo. L'accoppiamento con un PWR ed uno scambiatore di calore che brucia gas non è fattibile in quanto il sistema di riscaldamento dovrebbe fornire almeno 1.000 MWth. Il calcolo è molto approssimativo, dal momento che bilanci energetici del ciclo SI sono attualmente oggetto di studio, ed è impossibile prevedere esattamente quanta parte del riscaldamento potrebbe essere a carico del PWR. Tuttavia questo livello di approssimazione è sufficiente per scartare questa ipotesi.
Dall’analisi tecnica si ricavano:

- la taglia degli impianti presi in esame;
- dipendentemente dalla strategia operativa adottata, la quantità di elettricità/energia termica acquistate dall’impianto nucleare;
- la corrispondente produzione annuale di idrogeno.

Questi dati rappresentano gli input dell’analisi economica eseguita successivamente.

Prezzo medio dell’elettricità durante le ore di funzionamento a pieno carico e prezzo di vendita dell’idrogeno prodotto si rivelano le variabili chiave dell’investimento. In particolare, il prezzo dell’elettricità cambia anche sensibilmente da un anno al successivo [36], mentre per l’idrogeno non esiste un vero e proprio prezzo di mercato, poiché esso è prevalentemente prodotto e consumato ‘in situ’, e poco più del 5% della produzione globale è scambiata sul mercato [37].
Di conseguenza, la valutazione della fattibilità economica non può essere effettuata semplicemente attraverso il Valore Attuale Netto (NPV) calcolato a fine vita dell’impianto,

perché una variazione di uno dei due fattori sopracitati, renderebbe l’analisi inefficace. Per questa ragione, nella valutazione dell’investimento dell’impianto di WE, l’output dello studio è il prezzo di pareggio dell’idrogeno, rispetto ad un determinato scenario di costo dell’elettricità.

Partendo dai risultati di cui sopra, è stata eseguita la valutazione economica dei tre impianti. I principali risultati sono i seguenti:

- Il costo principale dell’elettrolisi dell’acqua è rappresentato dall’ energia elettrica. Ciò, unito alla grande flessibilità che caratterizza questa tecnologia, suggerisce che si possa trarre grande vantaggio dal far lavorare gli elettrolizzatori solo nelle ore ‘off-peak’, ossia quelle a minor costo dell’energia elettrica;
- L'idrogeno da WE può essere prodotto a prezzi relativamente bassi finché il prezzo dell'energia elettrica è molto basso (2 c €/kWh);
- Se il prezzo dell'elettricità è superiore a 2 c €/kWh, l’H_2 da elettrolisi dell'acqua non può competere con quello da Steam Reforming del Metano, a meno che non venga introdotta una carbon tax molto severa;
- Per tutti i prezzi dell'elettricità, la strategia BC 12 è più profittevole della BC 8. Una strategia operativa che prevede di destinare il 50 % della potenza di output di un NPP per ben 12 ore (anziché le più classiche 8) ad un impianto ausiliario è ai limiti rispetto alla definizione di Load Following. Tuttavia, trovando un accordo con i gestori del NPP e della rete, questa sarebbe un’opzione interessante;
- La modalità operativa FR dà un significativo valore aggiunto per l'investimento finché la sua velocità di degradazione dell’ efficienza è bassa (2% / anno);

Per quanto riguarda i due impianti HTSE e SI:

- L’impianto Zolfo-Iodio è potenzialmente competitivo anche per prezzi medio-alti dell’elettricità, se il prezzo dell’ idrogeno raggiunge 0,30 € / Nm3;
- Il SOEC diventa molto redditizio solo per i prezzi elevati di idrogeno (0,30 – 0,45 €/Nm^3), ma solo se il tasso di degradazione dell’efficienza rimane al di sotto del 5-10%/anno.

In ogni caso, prima di realizzare Load Following con tecnologie quali i SOEC e il ciclo termochimico Zolfo-Iodio, devono essere affrontate questioni non tecniche, ma anche normative, di licenze e di accettazione pubblica.

Per quanto riguarda l'accettabilità degli attuali costi dell'idrogeno, non può essere fatto un equo confronto tra idrogeno da elettrolisi dell'acqua e quello da Reforming del metano, perché:

- L'idrogeno da steam reforming del metano ha una purezza molto inferiore a quella ottenuta da WE, ed è usato principalmente per applicazioni industriali;
- L'H_2 da WE ha purezza molto elevata, quindi usarlo per i processi industriali è uno spreco; mentre l'alta purezza è richiesta dalle Fuel Cell.

In sostanza l'idrogeno da elettrolisi dell’acqua è un prodotto che ha bisogno di un mercato, che potrà essere costituito da un'ampia diffusione di veicoli a celle a combustibile.

1 Introduction

In the first decade of the XXI century has begun a 'nuclear renaissance', which after a slowdown suffered in the aftermath of Fukushima, seems to be now recovering [1], [2].

In these years the world population is growing rapidly, leading to an increase of the energy demand: the International Energy Agency (IEA) projects that global electricity demand will increase 2.2 percent a year to 2035 [3].

Moreover, the growing sensitivity to environmental issues that is being recently demonstrated even by countries as the United States[4], [5], which had not subscribed the Kyoto protocol of 1997, encourages increasingly constraining standards on emissions of harmful gases.

In this context Nuclear Power Plants (NPP) can be deployed along with renewable power plants to achieve the long term perspective of sustainable development, limiting the emission of greenhouse gasses.

The decision to follow this direction or not in the future concerns to the politicians of the most developed and developing countries. Anyway, nuclear power has right now a relevant share of the total electric power production, with more than 2,410 TWh produced in 2014 [6]; and considering the large number (counting both operating and under construction plants) of NPPs in the world [7], it will play an essential role also for a few decades, at least.

Furthermore, the power sources portfolio in several developed and developing countries is forcing the nuclear plants to follow the energy demand, and so to operate at variable power output [8].

As a consequence, nuclear reactors designers and owners have studied the capability of the plants to work in the so called ‘Load Following’ mode [8], reducing the power output, and then the overall electric energy produced during the nuclear plant lifetime.

Since a specific feature of the nuclear energy is the high incidence of the plant capital cost (60%, against, e.g. 15% for a turbogas, [9]), a reduction of the production represents a loss of revenues without involving a significant cost reduction because of the fuel saving.

In other words, the Load Following with nuclear power is an underutilisation of the plant.

This trend urges the scientific community to ever look for new technological solutions, to fully exploit the potential of a nuclear reactor.

1.1 Load Following with Nuclear Power Plants

1.1.1 Why Load Following?

Historically, Nuclear Power Plants (NPPs) have been mainly seen as a base-load source of energy [8].

This is the most economical and technically simple mode of operation: power changes are limited to frequency regulation for grid stability purposes, and shutdowns for safety purposes.

Still nowadays, the majority of NPPs are used for the base load, and operate at a fixed power level [10], but there is an increasing number of countries (e.g. France and Germany), where this situation has changed, and NPPs are forced to work in the Load Following mode [8].

For instance, in France the share of nuclear power in the national electric portfolio is so relevant (75% [8]), that is not possible to let all the nuclear plants work at full load all the time.

In the Figure 1-1 it can be seen how the nuclear power output in the French electricity market decreases during the night, and especially during the weekend, in a typical autumn week.

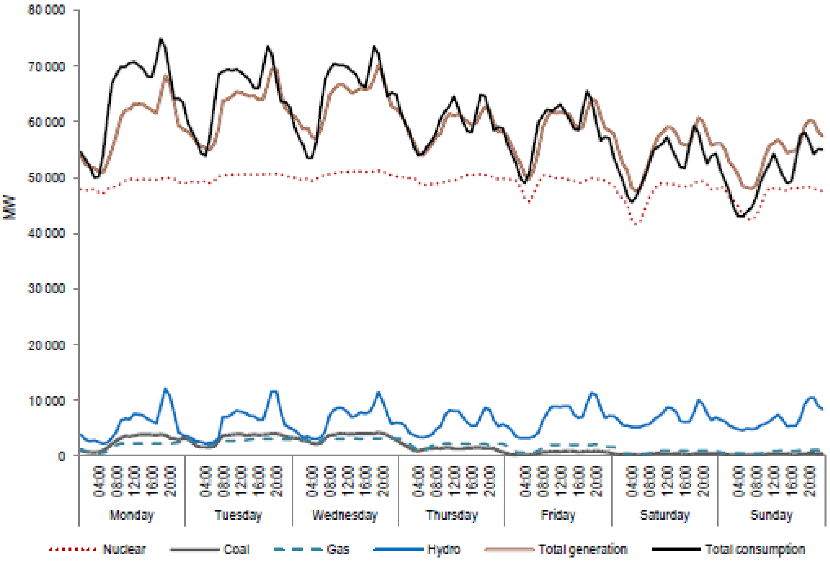
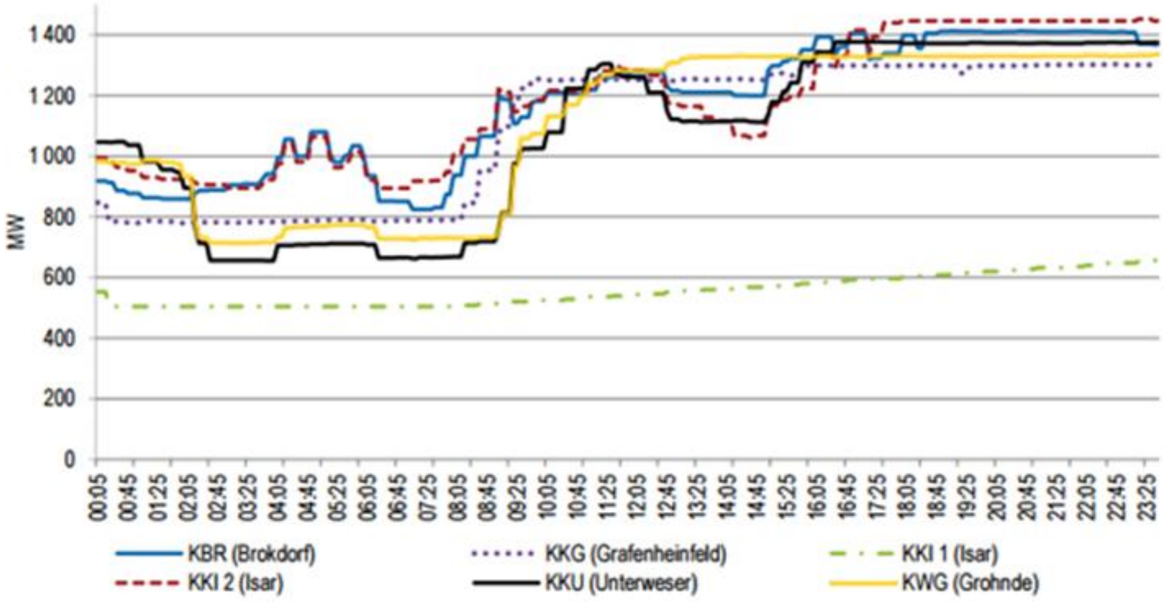


Figure 1-1: Exemple of electricity generation in France during two weeks in November 2010 [11]

Although France is an exception regarding its so large nuclear share of power production, several countries that present shares above 50%, namely Belgium, Hungary, Slovakia and Ukraine [6], may face the same problem.

Furthermore, even in countries not having a very high penetration of nuclear power (e.g. South Korea), the Load Following can be imposed by local grid balancing issues, in specific regions characterized by an heavy presence of NPPs.

There is another main reason why Nuclear Plants could be obliged to adopt Load Following: it occurs when in the same country (and so the same grid) an ever-increasing part of the installed power portfolio is constituted by large-scale deployment of intermittent and must-run sources of energy like PV or Wind (e.g. in Germany) [8].
Since these plants are not controllable, but operate only when sun and wind are present, in order the power supply not to exceed the demand, other plants have to reduce their power level.



Courtesy of E.ON Kernkraft

Figure 1-2: Example of the electricity generation with some German Nuclear Power Plants (PWR and BWR

Anyway, the power demand of a specific NPP is strongly dependent on the energetic portfolio of the geographic area where this last is collocated.

Figure 1-2 shows the power output of 6 NPPs operating in Germany.
It can be noticed that while all of them operate at full power during the 16.00 – 24.00 time period, their load factors are largely different during the remaining part of the day, and especially during the night when some operate approximately at 70 – 80%, and others (as Grohnde and Unterweser) at 50%; this is reasonably due to differences in the composition of power plants portfolio of the areas surrounding the considered NPPs.

This situation is forcing the utilities to implement or improve the manoeuvrability capabilities of their NPPs, to be able to adapt the electricity supply to daily or seasonal variations of the power demand (Load Following), as explained by [8].

The US Energy Information Administration defines the Load Following as: "*Regulation of the power output of electric generators within a prescribed area in response to changes in system frequency, tie line loading, or the relation of these to each other, so as to maintain* *the scheduled system frequency and/or established interchange with other areas within predetermined limits*"[38].

Generally speaking, a power plant can achieve regulation mainly in three ways:

- Increase and decrease the flow of fuel (e.g. gas, coal, oil);
- Energy storage: Pumped Hydroelectric Storage (PHS) and compressed air energy storage (CAES) ;
- Dissipation (e.g. inserting neutron absorbers into the core of a NPP).

The requirements for a NPP to perform Load Following (LF) are specified in [39], that in matter of load following reports:
"a unit must me capable of continuous operation between 50% and 100% of its nominal power (Pn), […]. Load scheduled variations (should be) *2 per day, 5 per week and 200 per year".*

Modern NPPs, like the LWRs operating in France, are designed to have a strong manoeuvring capability. More specifically:

- Cappolani et al. [11] state that slow ramps of < 1.5% P_N (Nominal Power) per minute are often used in France (by operating LWRs), and the typical low power level is about 50% P_N.
- The EPR satisfies better manoeuvrability requirements [40]:
  - it can perform LF between 25% and 100 % P_N;
  - and supports higher power variation speeds, until 5% P_N per minute.

Several French NPPs follow a variable load program, with one or two large power changes per day [8].
This can be made in different ways [8][9]:

- For PWRs: by inserting the control rods (made of neutron absorbers), or by varying the boric acid concentration in the primary coolant;
- For BWRs: by changing the coolant flow rate (by mean of recirculation pumps), or again with the control rods. No boric acid is used in BWR.

All these methods induce a decrease of the reactivity into the core, i.e. a variation of the produced thermal power, and so they modify the thermodynamic (TD) conditions in the primary (and then secondary) loop [9].
This introduces thermomechanical stresses in the primary loop, coupled by a slow but steady fatigue cycle. Even though this problem can be mitigated, if not avoided, by modern NPPs designs [8], the LF still essentially remains an underutilization of the plant.

Unlike for gas power plants, there is not a relevant cost saving in decreasing the electricity production, because [9]:

- Capital cost is a sunk cost;
- O&M costs (e.g. staf) are fixed and independent from the power rate;

- Nuclear fuel accounts for only about 10%-15% of generation costs.

Thus, the economic consequences of load-following are mainly related to the reduction of the load factor, which indirectly causes an increasing of the capital cost / energy produced ratio, resulting in a great waste of resources.

1.1.2 Operation modes in Nuclear Power Plants

There are four operation modes currently used by nuclear power plants:

- Base-load generation mode;
- Primary frequency control;
- Secondary frequency control;
- Load Following mode.

Base-Load Mode

In base-load operation mode, the nuclear power plants operate at constant nominal power during most of the time.

Primary and Secondary Frequency Control

The power demand can never be exactly evaluated in advance, thus there is a certain random variation of demand resulting in frequency fluctuations (as can be seen in Figure 1-3), typically of less than 20 mHz [8]. The power plants have to monitor the frequency on the grid and immediately adapt their level of generation in order to keep the frequency stable at the desired value. This kind of regulation is called *primary control*. The power modulations for the primary control in frequency regulation are performed in the interval of ±2% of P_N. In addition, the primary frequency control allows short-term adjustment of electricity production and demand in the time frame of about 2 to 30 seconds after the deviation is observed.

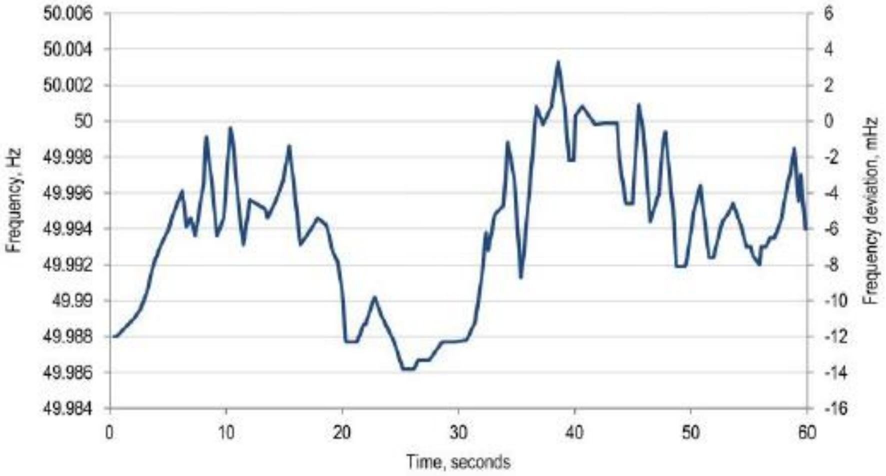


Figure 1-3: Example of the frequency variation on the grid in Europe. Target in Europe is fixed at 50 Hz

Another type of frequency regulation, named *secondary control*, acts over a longer timeframe (say, from several seconds to several minutes) and restores the exact frequency by calculating an average frequency deviation over a period of time. The secondary control is particularly important because of the interconnection of the grid of a country with other European grids. In order to adjust the frequency, taking into account the balance of electricity exchanges with other European grids, the grid operator sends a digital signal to the NPP to modify their power level in the interval of ±5% P_N [8].

Load Following

Nuclear power plants operating in load following mode follow a variable load program with one or two power changes over a period of 24 hours. The load pattern is determined by the grid operator and the utilities, depending on the power demand and the manoeuvring capabilities of the plant itself. Depending on the load pattern, several intervals of power ramps are authorised ranging from 1% of P_N per minute to approximately 5% of P_N per minute [8].

1.1.3 What is Cogeneration?

The EIA defines the Cogeneration as: *" production of electrical energy and another form of useful energy (such as heat or steam) through the sequential use of energy"* [38].

It essentially consists in a thermodynamically moreefficient use of fuel.

In any thermoelectrical plant, some energy must be discarded as waste heat (according to the second principle of TD), but in cogeneration this thermal energy is put to use.

All thermal power plants emit heat during electricity generation, which can be released into the natural environment through cooling towers, flue gas, or by other means. In contrast, cogenerative designed plants captures some or all of the waste heat, and use it as:

- hot water for district heating;
- process heat for medium-high temperature thermal application in various industrial plants.

1.1.4 Load Following by an Auxiliary Plant

The research field in which this thesis moves is based on a key idea: since the Load Following for Nuclear Plants is not avoidable, it can be found a way to perform it without wasting resources.

The basic idea of the 'Load Following by an Auxiliary Plant' is to merge the two concepts of Load Following and Cogeneration in a single operating strategy.

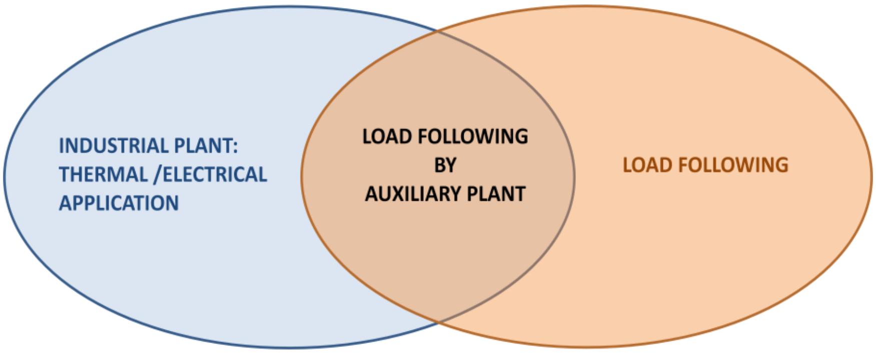


Figure 1-4: The basic reasearch idea: to perform Load Following by providing thermal / electrical enrgy to an Auxiliary Plant

The Nuclear Reactor works always at nominal power, leaving the primary circuit unchanged. During the high load hours (day) the NPP provides maximum electricity grid, while during hours of low demand (night) the not required electricity (or process heat) is directed to an industrial plant, which produces valuable by-products. This strategy is represented in Figure 1-5 , which represents in the yellow area the total produced that is required by the grid. The red area represents the 'excess energy' for the NPP, which is send to the Auxiliary Plant.

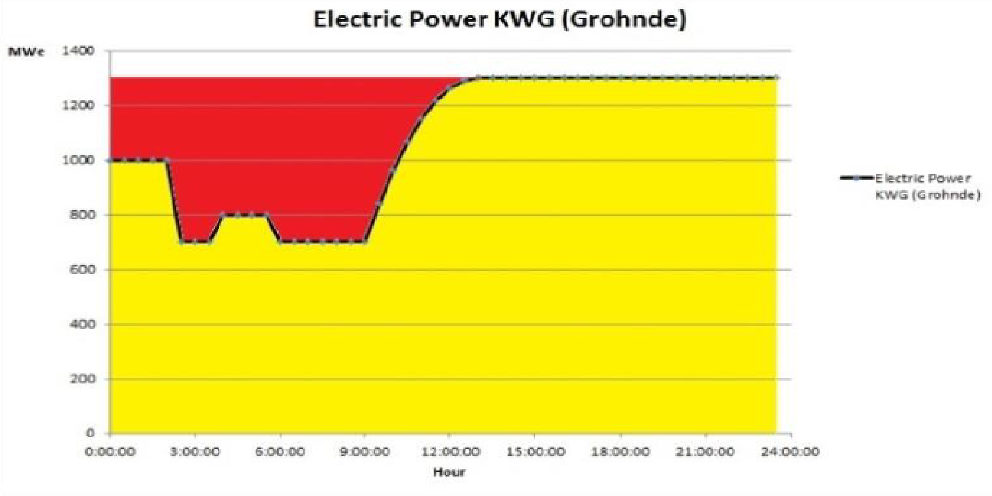


Figure 1-5: Yellow area: approximated electric energy actually supplied to the grid by Grohnde Plant (Germany), during a typical day. Red area: amount of energy available for the Auxiliary Plant in order to work in Load Following mode.

The coupling is particularly virtuous for those industrial installations which require a large amounts of energy as heat or electricity, and whose main cost of production is represented by the supply of these latter.

It must be underlined that while this concept has been borrowed by Cogenerative designs, technically speaking, it is inappropriate to speak of 'Load Following by Cogeneration', at least for electrical applications because:

- In an electrical application, all the waste heat is still expelled. This is probably the negative aspect of electrical applications with Nuclear, due to the very low thermodynamic (TD) efficiency of NPPs;

- On the contrary, in non-electrical applications, the whole (not required) thermal power is delivered to the Industrial Plant during the night, thus the waste heat is drastically reduced.

The most suitable not-electrical applications would mostly require low quality thermal energy. In this way, the heat is not converted through a not-efficient electric conversion [12].

This is the reason why non-electrical applications, even though more difficult to realize, are preferable, in a medium-long term scenario.

Before discussing the basic characteristics that are required by an Industrial Plant (with a thermal power demand) to be a candidate for the coupling with a NPP, it is presented a brief dissertation in order to explain which are the Nuclear Reactors best fitting this coupling.

1.1.4.1 Large Reactors vs Small- Modular Reactors

In the second half of the last century the efforts of nuclear engineering have focused on building power plants of larger and larger size: currently, reactors of around 1.5 GWe are designed and under construction (EPR, AP1000) , or already built (ABWR) [41].
This is due to the axiomatic application of the principle of economies of scale, according to which increasing the scale of production the average unit cost of the product decreases.
This principle, proved valid for any industrial plant, is more difficult to apply to the nuclear case, as explained by [42].
Economy of scale does apply only if the considered designs are very similar, as it has been the case in the past.
This is no longer true today, where smaller, modular reactors have very different designs and characteristics from the large ones. which is not the case of nuclear plants. This because reactors of greater size require complex changes to the design of the plant, larger and more expensive security systems, more time for licensing and for the construction [42], [43].

Over the past 10 years it has diffused through the scientific community a strong interest in a return to small-medium sized reactors (up to 300 MWe) [44], [45], possibly deployed in series in a single site, to reach the power of the existing facilities commercial size: from which the modular nature of these plants (Small Modular Reactors).
Several papers have shown that SMRs can be economically competitive with Large Reactors (LR), in certain scenarios and certain contexts.
Carelli [42] analyzes specific factors, such as grid characteristics, construction time, financial exposition, modularization, learning (economy of replication which substitutes economy of scale), which distinguish SMR from LR in the evaluation of the capital cost. He asserts that once having taken these factors into account, the capital cost reveals not to be a discriminator between the two technologies.
Locatelli et al. [43] discuss the effects of 'non financial parameters', such as electric grid vulnerability, public acceptance, risk associated with the project and others, on the

evaluation of the best reactor size for an investment in nuclear sector. For many of these parameters, they proved that SMRs show to have an advantage on LRs.

Even though is not clear when and if SMRs will actually be preferred to LRs, it is known that SMRs are much more suitable for thermal applications than LRs.
Indeed, as [12], [13] explain, NPPs are base-load technologies, designed (for technical and economic reasons) to work at full power.

Let us consider a 1,000 MWe (LR) PWR, with whom we want to perform Load Following during the night:

- The steam turbine (and its ancillary systems) are designed to maximise the efficiency at about the full power;
- If one assumes that during the night the steam is split in half with a cogeneration plant, it can be extracted before it enters the turbine, so the turbine is forced to work "off-design" , i.e. far from its maximum efficiency. This means a waste of 100-150MWe equivalent of power [13].

Now, let us compare this latter strategy to the one achievable with the SMRs. Let us assume that an owner of 4 SMRs PWR of (250 MWe each) want a 50% load during the night:

- 2 SMRs operate at full electrical power, with an output of 500 MWe, working at their maximum efficiency;

- 2 SMRs operate only to provide thermal energy to the auxiliary plant, getting a bit less of the maximum efficiency, to keep the turbine “spinning and warm”: about 7% of heat power lost on single plant; 3% on total [13].

For the reasons mentioned above, from now on, we take as a fact that for thermal applications SMRs are better than LRs from an economic standpoint.

1.1.4.2 Auxiliary Plants: Requirements for the coupling

The coupling with an electrical application is the most simple, because of several reasons:

- It does not require any modification within the NPP design, since its output remains exactly the same either if it is working for the grid, or the Auxiliary Plant.
- For the same reasons, no modification of the TD cycle are involved. This means that the energy is split in two parts outside of the NPP;
- No proximity between the Auxiliary Plant and the NPP is necessary, since Electric Energy (EE) can travel long distances with relatively small losses. Thus also licensing process should reasonably be easier and faster.

Essentially *every* plant which requires EE could be coupled with a Nuclear Plant; the matter is that:

- Its power demand must be very great (670 MWe, i.e. the half of 1,340 MWe, which is the nominal power of 4 PWR SMR modules);

- It has to be flexible to work at full power during the night, and stay off (or operate at a much lower load, consuming a reasonably small electric power) during the day.

Non-electrical possible applications need a more thorough treatment.
During the 1990's it started a program on the cogeneration with nuclear, which was primarily concerned with seawater desalination, and district and process heating. In recent years the aim of this program has been widened to include other more promising applications such as nuclear hydrogen production and higher temperature process heat applications [17].

Non electric applications of nuclear power may be foreseen for a wide range of applications such as hydrogen production, nuclear seawater desalination, district heating, oil recovery, coal conversion, and other industrial applications for the petrochemical and refinery process, paper and textile etc. It is evident that the specific temperature requirements for such non electric applications vary greatly from low (less than 100° C in case of heating) to very high (more than 1000° C in Iron and steel industry) [17].

Despite all industrial processes requiring process heat are hypothetically candidate, an auxiliary plant in order to be compatible with a NPP operating in LF mode, should:

- need a large thermal power (about 2,000 MWth, i.e. approximately 3 times the electric power output, taking into account the TD efficiency, or an equivalent combination of electrical and thermal);
- require relatively low temperature heat (except for the coupling with a HTGR, but currently the large majority of NPPs worldwide are PWR and BWR[9]) :
    - 300 °C with a PWR;
    - 400 °C with a SFR;
    - 900 °C with a VHTGR.
- do not have a high thermal inertia;
- lend itself to daily load variations, with rather fast dynamics.

The absence of the last two characteristics could permit the Cogeneration, but it would impede the Load Following operation.
In fact, the aim would be to operate the auxiliary facility at full load during the night, and turn it off or let it work at the minimum possible load (anyway low) for the remaining part of the day, when selling electricity is the priority.
It is clear that in order to lend itself to operations of this type, the plant must have characteristic times of the load variations of a few minutes, tens of minutes at the most.

In Figure 1-6, the required temperatures for a variety of industrial processes are presented.
Some of these coupling have already been considered and studied, as we will see in the section 1.2.

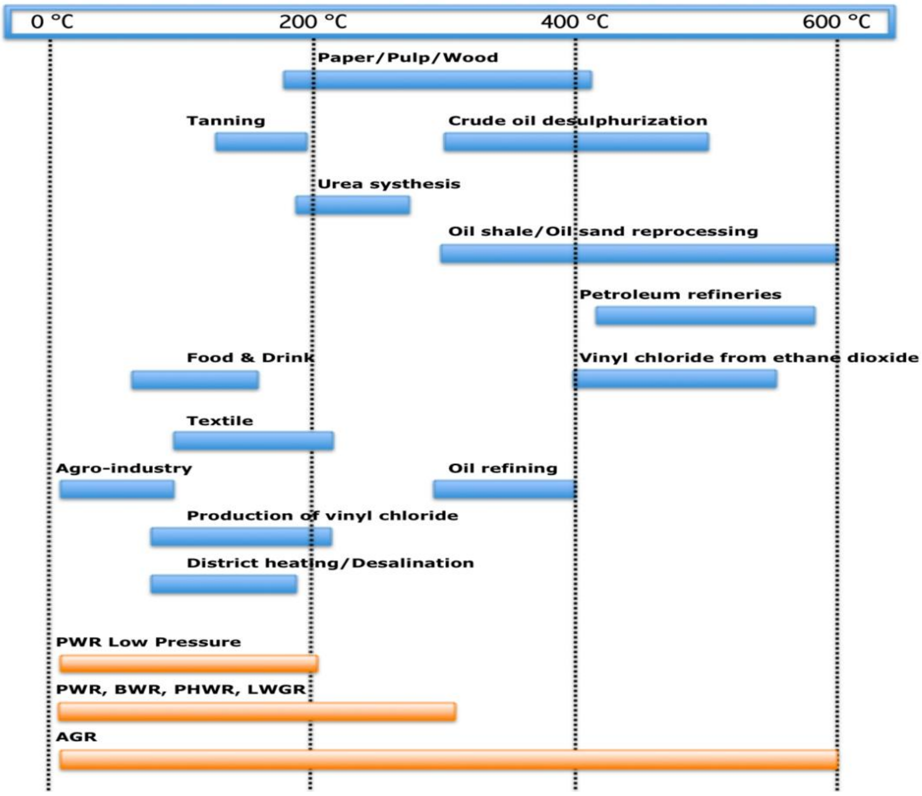


Figure 1-6: Required temperatures for industrial processes and reactor types

1.2 Cogeneration and Load Following with Nuclear Power

About one-fifth of the world's energy consumption is used for electricity generation, and today nuclear energy contributes approximately 15.2% of the world's electricity [18]. Most of the world's energy consumption is for heat and transportation. Through advanced applications, nuclear energy has considerable potential to penetrate these energy sectors now served by fossil fuels that are characterized by price volatility, finite supply, and environmental concerns.

Although a few commercial nuclear power plants world-wide provide energy to non-electrical applications, nuclear energy is primarily used only for base-load electricity production. Of the nominally 440 commercial nuclear plants operational world-wide, 59 units in 9 different countries (Bulgaria, Czech Republic, Hungary, India, Romania, Russia, Slovakia, Switzerland, Ukraine) are being used for district heating and 12 units in 3 countries (India, Japan, Pakistan) are being used for water desalination [18]. To date, no commercial reactor plant has been used to provide process heat directly to industrial applications such as oil refining or chemical production [46].

1.2.1 Seawater Desalination

Together with pollution and depletion of hydrocarbon resources, water scarcity is one of the most serious global challenges of our time. The challenge of providing ample and safe drinking water is further complicated by population growth, industrialization, contamination of available freshwater resources, and climate change. Nuclear energy can make a substantial contribution to the challenge of providing ample and safe drinking water to everybody, providing energy to desalination plants [17].

Desalination has decisively proven during last 30 years its reliability to deliver large quantities of fresh water from the sea. Unlike oil, fresh water has no viable substitute. The sea is the unlimited source to create new fresh water through desalination [17].

Currently about 2.3 billion people live in water-stressed areas and among them 1.7 billion live in water-scarce areas, where the water availability per person is less than 1000 m^3/year [17].

In some countries water desalination is a reality: Qatar and Kuwait rely 100% on desalinated water for domestic and industrial supplies. Furthermore the desalination capacity is increasing in the Middle Est and Africa [47].

Desalination processes could be classified essentially in two groups: thermal processes and membrane processes [12]:

- Thermal processes consist in causing evaporation of water and subsequent re-condensation of steam, once it is salt-free.
- Membrane technology is based on the separation of salts using their physical-chemical properties.

Thermal processes require mostly thermal energy (low temperature steam), while membrane facilities require only electricity.

Nowadays, half of the total desalination investments are addressed to Seawater Reverse Osmosis (SWRO) projects, due mainly to its lower overnight and total water costs compared to other conventional processes [12].

Many efforts have been done to prove and confirm a good suitability of a cogeneration between a nuclear power plant and a desalination facility [26]–[29]. Over 200 reactor-years of operating experience on nuclear desalination have been accumulated worldwide [18].

Locatelli et al. demonstrate that a desalination plant is flexible enough to be coupled with a nuclear power source; moreover the required size of the considered plant has revealed to be similar to the largest plants worldwide [13].

Moreover, [13] provides a curve representing the breakeven water price varying the electricity price (Figure 1-7). Thus, in a certain scenario, starting from a certain water and electricity prices (including the typical spread day/night), one can assess if the investment in a desalination plant is:

- Profitable, for 24 h/day production;
- Non-profitable;
- Or profitable, just operating for a certain number of hours per day.

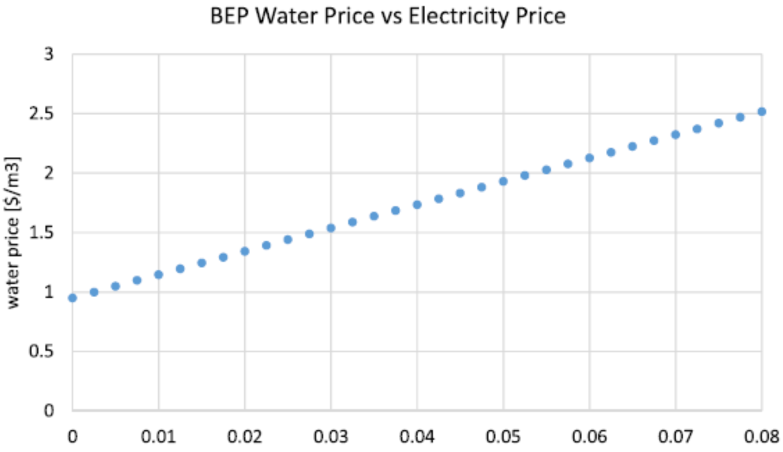


Figure 1-7: Breakeven price of desalinated water, varying the Electricity Price [13]

Anyway, [18] points out that those countries suffering from scarcity of water do not generally have nuclear power plants, and do not have a nuclear power infrastructure. The utilization of nuclear energy in those countries will require infrastructure building and institutional arrangements for such things as financing, liability, safeguards, safety, and security and will also require addressing the acquisition of fresh fuel and the management of spent fuel.

Finally, it should also be underlined that not all the countries that are supposed to be forced to make the NPPs work in Load Following mode (and actually not many among them), do not need desalinated water. So, the research for an auxiliary plant suitable for Load Following remains open.

1.2.2 Gasoline

Raw crude oil unuseful in industrial applications, since low viscosity, low sulfur, … are required.

Thus, a separation process, called refinery, is performed.

Crude oil is heated and separated by evaporation into fractions by fractional distillation.

Valuable products are obtained in this way, such as gasoline, diesel, kerosene, etc.

Figure 1-8 shows the refining process: the crude oil is heated and vaporized passing through a furnace. Then it enters the fractioning column and begins to climb and cool down: the heavyer substances condensate at higher temperatures, then fall and are collected, while the lighter continue to climb and cool.

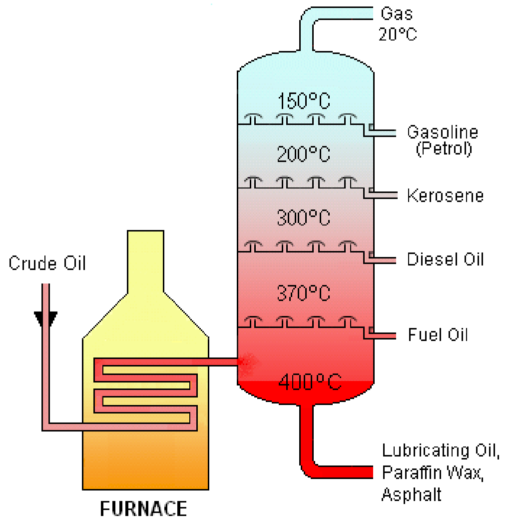


Figure 1-8: Crude Oil refining process scheme

Alonso [19] suggest that steam process (coming from an helium cooled high temperature nuclear reactor, PBMR) can be used to heat crude oil. He proposes to use 65 MWe (over 165) for steam production.

According to [19] from a technical standpoint the steam process production is more suitable using the PBMR because the gas temperature is higher than the one coming from the Gas turbine in the Combined Cycle, which increases the thermal heat transfer providing more compact equipment for the process in the PBMR than in the combined cycle using natural gas.

The results show that process steam using a PBMR is not economically competitive against combined cycle gas turbine plants under an scenario of 5% discount rate and 5 US$/mmBTU and no cost for CO2emissions [19].

To be competitive, it would be necessary a discount rate of 10% and cost for emissions at least of 60 US$/ton of CO_2,which, Alonso notices, seems very unlikely.

1.2.3 Shale Oil Extraction

As Curtis et al. [51] explain the U.S. has the largest and most concentrated oil shale formations in the world. U.S. resources are estimated at about 2 trillion barrels of oil.

Oil shale contains kerogen, but no liquid oil. So the process basically consists in heating oil shale underground to ~330°C converts the kerogen to a light high-value oil, natural gas, and char, and then to extract these products, as shown in Figure 1-9.

The energy required is enormous: in non-nuclear processes the 25% of the product is burnt for the heating [51].

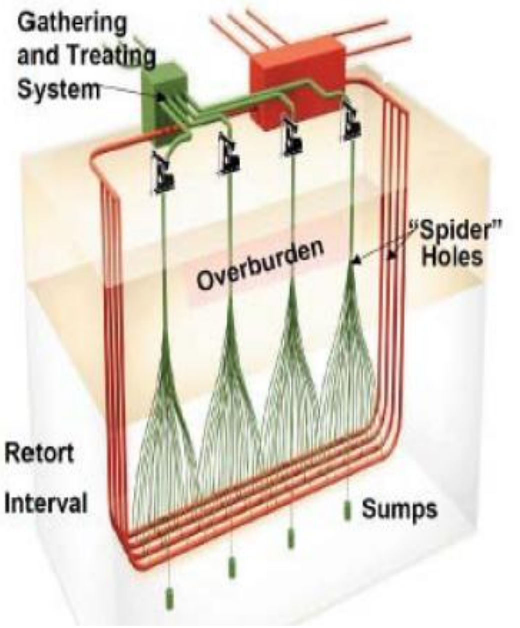


Figure 1-9: Shale Oil extraction process

Curtis et al. [51], [22] suggest the use of the Nuclear Renewable Oil Shale System (NROSS) to heat the steam which is sent in the subsoil.
In this case the oil shale would be heated to between 210 and 250°C using closed steam heating lines, and then a further heating of the steam(to 370°C) would be made by electric heaters.

They assert that the resource is sufficiently dense for a full-size reactor to supply steam for a 60 year lifetime within a 2 km radius.
Moreover the low conductivity rock would permit to provide the energy could only during low electricity demand hours, so constant heating would not be required.

Finally, if the statements made by [51] are confirmed, Oil Shale extraction could be a suitable application for the Load Following with Nuclear Power.
Anyway it must be said that some previsions, especially regarding the 60 years of continuous energy supply from the NPP, seem optimistic. In case of less operation time on a site, NPPs capable of moving from one site to another would be required, and this would recall into question the investment.

1.2.4 Algae – Biofuel

Excessive consumption of fossil fuels, particularly in large urban areas, has resulted in generation of high levels of pollution during the last few decades. Fossil fuels are the largest contributor of greenhouse gases (GHGs) to the biosphere [52]. Furthermore, it is well known that their combustion releases in the air a sizable quantity of particulates and nitrate oxides (NOx) [53].
In this context, countries across the globe developed state policies toward the increased and economic utilization of biomass for meeting their future energy demands, in order to meet the target of a carbon dioxide reduction of 5.2% from 1990 values, as specified in the Kyoto

Protocol of 1997 [54] as well as to decrease reliance and dependence on the supply of fossil fuels .

A biorefinery is a plant whose input are mainly biomass, thermal and electrical energies and whose output is one or more types of biofuel [12].
Many types of biomasses are used to produce biofuels, the literature divides them in three generations [13]:

- first generation is composed by conventional crops (corn, soybean, rapeseed, sugarcane, etc.),
- second generation is composed by lignocellulosic biomasses (mainly forestry and agricultural waste),
- third generation is represented by innovative feedstock among which the most promising are microalgae [55].

Locatelli et al. propose a biorefinery plant for the coupling with a NPP according to the Load Following strategy. They explains that the fermenter is the most viable option for the microalgae cultivation, since all other technologies require much space (thousands of hectares) for a reasonable coupling with a plant, that has an installed power in the order of magnitude of GW [12].

Anyway, they conclude that a fermenter biorefinery must be operated on a continuous base, because of the perishability of the biomass and because the most significant power requirements are in the first steps of the production chain that have to be considered a continuous process . Consequently, the biorefinery is not suitable for the Load Following [13].

1.2.5 District heating

District heat involves the supply of hot water through a district heating system, which consists of thermal power plants (usually as cogeneration from electricity) and a network of distribution and return pipes.

In many countries, such as central and northern European countries and countries in transition economies, district heat has been widely used for decades.
District heating has the following technical requirements [18]:

- It requires a heat distribution network to transport steam or hot water in a typical temperature range of 80-150°C;
- Owing to higher losses over longer transmission distances, the heat source must be relatively close to the customer, typically within 10–15 km;
- The district heat generation capacities are determined by the collective demands of the customers. In large cities a capacity of 600–1,200 MWth is normal. The demand is much lower in small communities;
- The annual load factor is normally not higher than 50%, since heat is supplied only in the colder part of the year;

- To assure a reliable supply of heat, a backup capacity is required.

Coal and gas currently dominate the fuels used for district heating, several countries (Bulgaria, China, Czech Republic, Hungary, Romania, the Russian Federation, Slovakia, Sweden, Switzerland and Ukraine) already have experience in nuclear cogeneration for district heating (, so the technical aspects can be considered well proven [18].

Applying the Load Following strategy to the district heating is not possible, because it would clearly cause problems of social acceptability: it is unthinkable to provide hot water to the customers just during the night hours.

1.2.6 Summary Table on technologies

In Table 1-1 the main results of the literature review regarding the Load Following with Nuclear Power by the technologies discussed above, are summerized in terms of technical and economic feasibility.

	Technical Feasibility	**Economic Feasibility**	**References**
1.Seawater desalination	Yes	Yes	Several: [14]–[16],[17], [18]
2. Gasoline (petroleum refining)	Yes	Not	[19]
3. Oil shale extraction	Yes, but necessity of moveable reactors!	Under investigation	[20]–[22]
4. Algae-Biofuel	Yes (Cogeneration), but No LF	No LF	[12], [13]
5. District heating	Yes	Yes (for cogeneration); BUT load following is impossible (social unacceptableness)	[23]

Table 1-1: Summary of Load Following and Cogeneration technologies with Nuclear Power

1.3 The Research Goal: Preliminary Analysis

The candidates industrial plants that have been considered are:

- A pyrolysis reactor of plastic waste, for the production of diesel-like fuels;
- A plant producing pellets, obtained from processing wood waste;
- An hydrogen production plant.

Firstly, an overview of the technology is presented (with the exception of hydrogen that is treated separately in the following chapter).
Then, this step of the study tries to the answer to the following questions:

1. What is the typical size of the plant?
2. Would it be technically feasible to build a plant of 2,000 MWth equivalent?
3. Is there enough feedstock for this plant to be coupled with a NPP?
4. Would it be enough demand for the obtained by-product?

If the answer of the last three questions is yes (or at least it is uncertain) , then it is possible to proceed with a further step of the analysis, and face technical questions about the sizing, the dynamics, and finally perform the economic assessment. Otherwise, the analysis on performing Load Following with a NPP by this plant stops here.

1.3.1 Plastic Pyrolysis: why not?

1.3.1.1 Plastic pyrolysis process

During the XX century plastics have become an indispensable ingredient. They are non-biodegradable polymers mostly made of carbon, hydrogen, and some other elements such as chlorine and nitrogen. The consumes of plastics have strongly increased in the last decades, and because of their non bio degradability, plastic materials contribute significantly to the problem of Municipal Waste Management [56].
Because of the reasons above, the collect and recycling of the plastics is a relevant environmental issue.

Kumar reviews the four possible approaches regarding the plastics recycling [56]:

1. *Primary recycling*: it is realized with clean, uncontaminated, single-type waste. It is characterized by simplicity and low cost. The products of this process have quality comparable with original products made from virgin plastics;
2. *Secondary recycling*: This treatment is destined to waste plastics which are converted into lower quality products. There are basically two approaches: to separate plastics from contaminants, and then to segregate plastics into generic types, or to separate plastics from contaminants and to remelt them as a mixture, without segregation;

3. *Tertiary recycling*: it is chemical recycling. Plastic materials are converted into smaller molecules, which are reused in other chemical processes . They are: Chemolysis, Hydrolysis, Alcoholysis, Glycolysis, Methanolysis, Gasification, Cracking (or Pyrolysis).
4. *Quaternary recycling*: it includes the recovery of the energy content of plastic wastes. This is the last in order of preference between the recycling possibilities. Anyway, despite the environmental issues which remains open, incineration (combustion) aimed at the recovery of energy is currently the most effective way to reduce the volume of organic material.

Even though the first two recycling approaches are preferable, not all the collected plastics can recycled into new plastics.

Waste to energy has been a significant way to utilize the waste sustainably, simultaneously add to meet the energy demand. Plastics being petrochemical products have high calorific value, thus they can be converted back to useful energy, by mean of tertiary recycling processes [56].

In particular, Pyrolysis is the thermal degradation of waste in an oxygen-starved environment in which the oxygen content is low for gasification to take place.

Catalytic Pyrolysis is a non-combustion heat treatment that chemically decomposes waste material by applying heat, directly or indirectly to the waste material in an oxygen free environment.

These processes are endothermic, and the required energy is typically applied indirectly through the walls of the reactor into which the waste material is fed [24].

Several papers reporting a large variety of results of experiments conducted on laboratory scale are present in literature, including [57]–[59].

However, some general observations can be made:

- Pyrolysis is an especially appropriate recycling technique for waste streams containing different plastics and other materials, for which mechanical recycling is not feasible [60];
- Chemical nature of the plastic feedstock, reactor design, maximum temperature achieved, residence time and heating rate strongly influences the nature, phase and yields of the products;
- The parameter which mostly determines the output is the temperature: approximately 500 ◦C has been proved to be the best temperature in terms of both conversion and quality of the products [60];
- Secondly, it comes the effect of time: 15–30 min is generally the reaction time range [60];
- Independently of the heating rate, the catalytic pyrolysis leads to higher yields of gas than thermal degradation, independently of the type of blend and heating rate [61].

1.3.1.2 Plastic Waste Pyrolysis Criticalities

In 2012, out of 25 Mtonne of generated plastic waste, 6.6 M tonne have been recycled in Europe [25], and approximately 8.9 Mtonne have been reused for Energy Recovery.

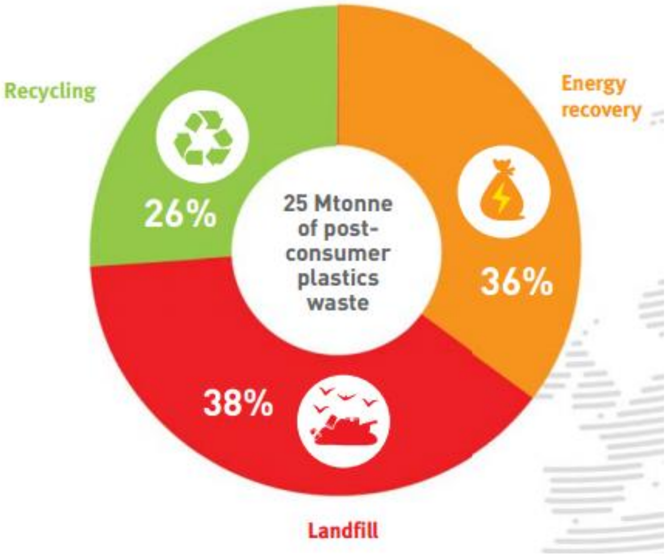


Figure 1-10: EU plastic waste generation in 2012

Nowadays, plastic pyrolysis is a niche technology, so almost the whole of the Energy Recovery is represented by Incineration, and even if the share of pyrolysis raise, it remains a certain quote of plastic which cannot be subject of any treatment, exept for incineration.

Anyway, supposing that pyrolysis could totally replace incineration, and that it is logistically feasible to bring all the collected plastic waste in Europe to a unique plant, what power input would this plant need?
It is not simple to answer this question; indeed, while there are some plastic pyrolysis pilot plants in the world (one the largest plant has a size of 20,000 tonne/year of processed feedstock: Akron, Ohio [62]), no one owner shares the data about power consumption. Moreover the facilities which perform experiment at laboratory scale requires few power (without keeping the account of the energy consumed).
Finally, the energy input from the process has been referred by a researcher interested in this field ([63] 3.), : approximately 6 MJ/kg (= $6*10^6$ GJ/Mtonne).

This means that a total energy of:

$$Annual\ Required\ Energy = 6 * 10^6 * 8.9 = \left[\frac{GJ}{Mtonne}\right][Mtonne] = 53.4 * 10^6 GJ$$
$$= 14{,}833\ GWh$$

Proportionally, a plant like Akron [62] approximately requires 33 GWh per year.
Considering that a NPP would discharge 5,548 GWh thermal equivalent (calculated from [35] data, see Table 3-1) during 1 year, the request for pyrolyzing the whole plastic for Energy Recovering in Europe, would be satisfied by less than 3 NPPs.

It should be noted some aspects:

- Plastic cannot travel for thousands of km, so it has to be consumed within a limited geographical area. At least 50--100 of this plants in Europe (considering one of this plants each 5 or 10 millions of citizens);
- Pyrolysis reactors are sophisticated and do not easily process inhomogeneous mixtures of different plastics, as plastic waste are ([63] 1.);
- Since the feedstock is not homogeneous, a perfect steady state is never achieved: this uncertainty on the feedstock makes the reactor not flexible, from the power input point of view ([63] 1.).

Thus, plastic pyrolysis is not feasible for the coupling with a NPP.

1.3.2 Wood Pelletisation – Steam exploded pellets: why not?

1.3.2.1 Pelletisation process

Pellet fuels (or pellets) are fuels obtained from compressed organic matter, or, biomass. They are generally made from compacted sawdust and related industrial wastes from the milling of lumber, manufacture of wood products and furniture, and construction.

According to [64] large volumes of pellets are nowadays produced for the large scale generation of heat and power, in order to replace coal with sustainable energy resources.

The manufacturing process of wood pellets consists of [65] grinding and refining (if required, depending on the feedstock), drying, size reducing, pelletizing (pressing), cooling and then screening and packaging .

Among these processes, the most significant from the energetic point of view are drying (thermal energy), and the pressing, for which it is necessary electrical energy.

Raw biomass presents some problems, including:

- High moisture content , and tendency to absorbs further moisture (which affects the integrity of the pellet);
- Bulky with low energy density;
- Degrades on storage;
- Fibrous and hard to reduce to small particle sizes;
- Irregular particle size and shape.

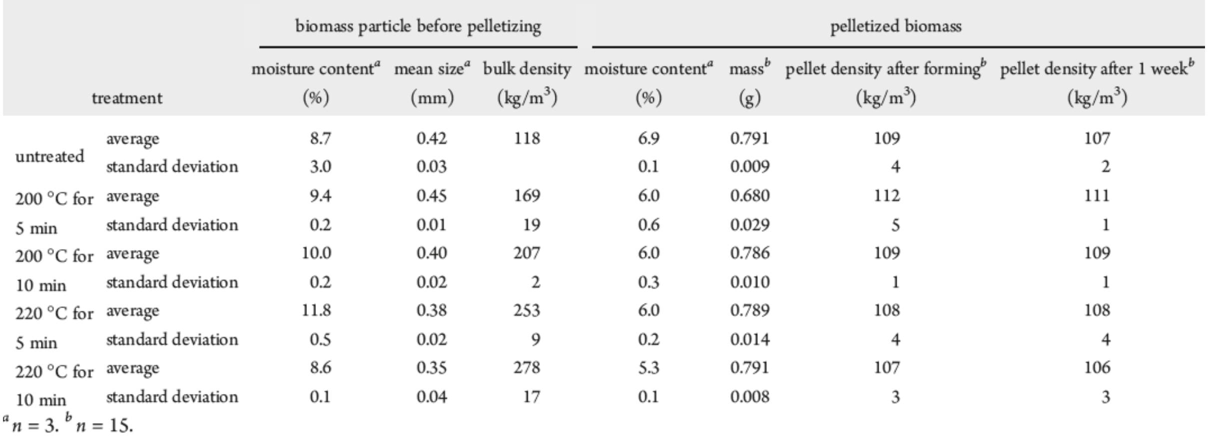
The Steam Explosion treatment offers solutions to many of these problems.

Basically this process consists in exposing the lignocellulosic material to high pressure steam for some minutes, before a very rapid decompression, which causes an ‘explosion’ of the steam inside the matrix. The defibrillation of the structure causes the depolymerisation of the lignine [66], [67].

In this way the less energetic part of the lignine is separated and eliminated.

The biomass retains the most of its energy content, with a partial loss of mass. This results in an enhanced energy density.

Lam [66] compares the properties of Pelletized biomass made of untreated and steam exploded (with 200 /220 °C steam and 5/10 minutes of residence time) material: as can be seen in Figure 1-11, the density is superior in the Steam Explosion case, and also its decrease with time is slower.



treatment		biomass particle before pelletizing: moisture content[a] (%)	mean size[a] (mm)	bulk density (kg/m^3)	pelletized biomass: moisture content[a] (%)	mass[b] (g)	pellet density after forming[b] (kg/m^3)	pellet density after 1 week[b] (kg/m^3)
untreated	average	8.7	0.42	118	6.9	0.791	109	107
	standard deviation	3.0	0.03		0.1	0.009	4	2
200 °C for 5 min	average	9.4	0.45	169	6.0	0.680	112	111
	standard deviation	0.2	0.01	19	0.6	0.029	5	1
200 °C for 10 min	average	10.0	0.40	207	6.0	0.786	109	109
	standard deviation	0.2	0.02	2	0.3	0.010	1	1
220 °C for 5 min	average	11.8	0.38	253	6.0	0.789	108	108
	standard deviation	0.5	0.02	9	0.2	0.014	4	4
220 °C for 10 min	average	8.6	0.35	278	5.3	0.791	107	106
	standard deviation	0.1	0.04	17	0.1	0.008	3	3

[a] $n = 3$. [b] $n = 15$.

Figure 1-11: Moisture content and Mean Size of Particles prior to Pelletization and Particle Moisture Content and Pellet mass and dimensions after pelletization. [66]

Despite of being an interesting application, steam explosion is not used on a large scale, because of the difficulty (in terms of energetic and machinery costs) to produce the required steam.

1.3.2.2 Wood Pelletisation criticalities

All over the world there is a huge wood pellets production: only in North America 13 plants, for a total capacity of 2.9 Mtonne per year are currently under construction [26]; adding this to the already operating plants, a total plant capacity of over 22 Mtonne/year is reached. The most part of these plants have sizes ranging between 10,000 and 400,000 tonne/year, but even larger ones are present; the largest one is in Waycross, GA (owned by RWE Innogy Cogen): 825,000 tonne/year.

As for the power consumptions, the companies which handle large plants do not easily give these data, nevertheless an Italian company operating in this sector with a medium size plant (120,000 tonne/year) shared its technical data, which are presented in Table 1-2 ([63] , 9.) :

Production (Output)	120,000	tonne / y
Grinding	0.25	Mwe
Refining, (mills)	0.7	Mwe
Drying	13.7	MWth
Sieving	0.53	MWe
Pelletizing	1.05	MWe
Packing	0.03	MWe

Table 1-2: Power input for each pelletisation process step (medium size plant) ([63] 8., 9.)

Starting from this, the total power inputs (thermal and electric) are simply obtained by mean of a sum:

Thermal Power	13.7	MWth
Electric Power	2.56	MWe
Annual Th Energy required	120	GWh_th
Annual El Energy required	22.4	GWh_e

Table 1-3: Thermal and Electric Power Input and annual Energy consumed (medium size plant)

Then, scaling up to the 1 Mtonne/year size, is made by a proportion. Clearly this is an approximated calculation, but at this step of the analysis the aim is to find the order of magnitude of the energy and required by this kind of plant. A clarification is relevant: in Table 1-4, the required energy is simply obtained by proportion, while for the Power it has been considered that the plant would operate just for 8 hours per day (night production, Load Following mode):

Thermal Power	343	MWth
Electric Power	64	MWe
Annual Th Energy required	1,000	GWh_th
Annual El Energy required	187	GWh_e

Table 1-4: Thermal and Electric Power Input and annual Energy consumed (Large size plant)

The thermal equivalent annual total energy required is then:

$$Annual\ Required\ Energy = Thermal\ Enrgy + \frac{Electric\ Energy}{thermal\ efficiency} =$$

$$= 1{,}000 + \frac{187}{33.5\%} = 1{,}558\ \ GWh_{thermal\ \ equivalent}$$

This value is still almost 4 times less than the excess energy from the NPP.

Moreover, even though there is no evident technical limit preventing the possibility to build pelletisation plant larger than 1 Mtonne/year, the companies consider this size as the maximum achievable, because of logistic issues, related to the waste wood procurement ([63] 8.).

Indeed, the wood present in forests is a valuable material and is used for the manufacture of furniture and other objects, of course not for pelletizing.

The raw material used in these plants is waste wood of carpenters. Given that the value added by the process in terms of energy is relatively low, the key factor for the economic profitability of the pellet is represented by the logistics and procurement of the lumber: collect and make the wood travel too much (technicians ([63] , 9.) estimate about 30—40 km at most) before processing it, means that transport costs outweigh the possible revenues. For this reason, these plants are placed at the center of very large districts of woodworking, and their size is limited by the amount of waste material present, more than by other technical considerations ([63] , 9.).

The considerations about the difficulties in the feedstock procurement remains valid for the Steam Exploded Pellets, whose energy consumption are reasonably slightly superior (because of the necessity to generate steam from water), but whose data are available just at laboratory scale [66].

Furthermore, also the licensing an social acceptability for a very large industrial plant that should be planted in great forests, which are often environmentally protected areas, are aspects that should be taken into account, especially if this plant should be coupled with a Nuclear Reactor.

For the reasons above, despite Pellets Plants show a significant power need, and good characteristics of flexibility, they are not suitable for the Load Following with Nuclear Power.

1.3.3 Hydrogen: why yes?

In industrialized and developing countries, motor vehicle emissions are major contributors to low urban air quality. According to [27], Hydrogen is one of the clean fuel options for reducing motor vehicle emissions, in the near future.

Nowadays there is already a large hydrogen production worldwide: 50 million tonnes per year [18], which roughly corresponds to 560 billions of Nm^3.

The main hydrogen consumer, divided by geographical area are [68]:

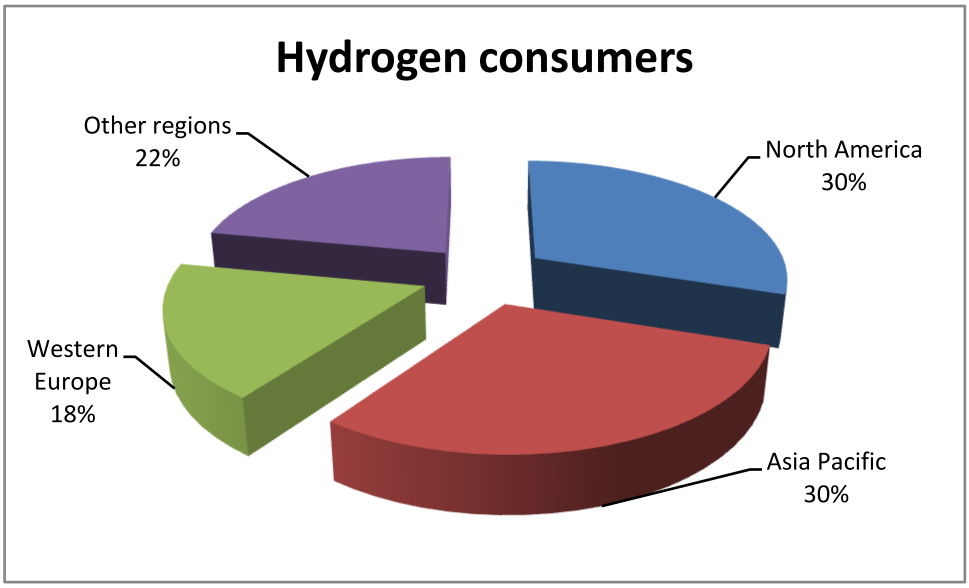


Figure 1-12: Hydrogen consumption share by geographical area

Although current use of hydrogen in energy systems is limited, its future use could become enormous, especially if fuel-cell vehicles would be deployed on a large commercial scale [69]. The hydrogen economy is getting higher visibility and stronger political support in several parts of the world [17].

As observed in [18], it is an attractive energy carrier that might play a major role in energy systems for many economic sectors in the long term.
Nowadays H_2 finds many applications as a chemical product for [18]:

- Ammonia (NH_3) synthesis;
- Methanol synthesis;
- Direct reduction of iron ore;
- Fossil fuel processing (hydro cracking);
- Fischer-Tropsch hydrocarbon synthesis;
- Methanation in long-distance energy transportation;
- Hydro-gasification.

Among them the most important applications are the production of Ammonia, which as fertilizer contributes to the essential nutritional needs of terrestrial organisms (146 Mtonne produced worldwide in 2006 [68]) and Petroleum Industry.
In addition, [18] states that there may be hydrogen markets for heating, stationary fuel cells, combined heat and power, and stationary gas turbines. Potentially hydrogen could be used for ground transport, aviation, marine applications, and railroad transport.

If the whole hydrogen was produced by water electrolysis, taking an Energy Input of 48.2 MWh/tonne_H_2 [69], (the origin of the values used in this section is justified in the following sections: 2.2.4 and 3.3 of this thesis); this means that it would be necessary $2.41*10^6$ GWh of electricity to produce it.
Considering a 1 GW-size NPP that produces 8,322 GWh of electric energy during 1 year, there could be 290 NPPs in the world, producing electricity 24 hours per day to supply the request of hydrogen. If we consider to use them just to produce hydrogen in the LF mode, so providing only half of its output power and only during the night (8 hours per day, e.g.), this number could be roughly multiplied for 6: it makes 1,740 NPPs 1GW-size. If only the 1% of total hydrogen production would be made by Load Following with nuclear power, then still over 17 NPPs would be required.

This simple calculations prove that there is enough hydrogen demand in the world, even today, to justify an hydrogen production plant of any size. Furthermore since the processes that are contemplated in this thesis obtain hydrogen from water, the potential feedstock can be considerate infinite. Once clarified this, it is also evident that before planting a real hydrogen plant in a site, the problem of how to dispose all the production:

- analyzing the needs of the industrial area surrounding the plant, if the hydrogen is supposed to be sold;
- otherwise properly sizing a further industrial plant, served by the hydrogen one.

2 Literature Review on Hydrogen

2.1 Introduction to Hydrogen

In the last decades not only scientists, but also the public opinion has been exposed to the concept that hydrogen would have played a key role in the XXI century.
It is seen as the most promising alternative to the gasoline for the private mobility [70], [71]. Furthermore since it composes the water, it is very abundant on the Earth, so one could think that an infinite source of energy is available for everybody. Clearly, this is not correct.
Hydrogen can be used as a fuel only in H_2 form; so it is necessary to *separate* it from the oxygen, according to the following reaction.

$$2H_2O + energy \rightarrow 2H_2 + O_2$$

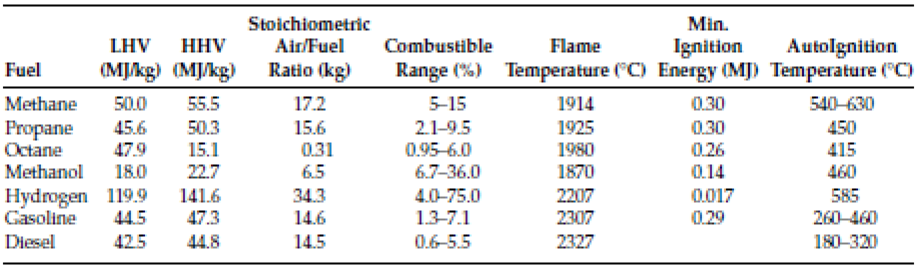
Firstly we have to highlight an important concept: hydrogen is not a *source* of energy. It is not naturally available as a ready to use substance. It must be produced, with a certain expense of energy.

Hydrogen is an *energy carrier*. It is a way to *store* energy in the chemical energy form, to transport it, and then to use it when and where it is needed: this is its great value. Similar to electricity, hydrogen is a high-quality energy carrier, which can be used with a high efficiency and zero or near-zero emissions at the point of use [34].
In accordance with the second law of thermodynamics, then, the energy generated by the combustion of H_2 can be at most equal to that consumed to produce it; actually it will be much lower because of the variety of losses that are involved in these processes.

2.1.1 Physical and Chemical Properties

Hydrogen is the lightest and most abundant element in nature: 75%wt of the visible matter in the universe is constituted by hydrogen [68].
Its atomic structure is constituted by a nucleus (with a single proton), around which orbits one electron.
At standard temperature and pressure hydrogen is generally not toxic, but poses a risk of asphyxiation if inhaled. Because hydrogen gas is odorless, tasteless, and invisible to human beings [72].
Hydrogen gas has the smallest molecular size compared to all other gases; its specific weight is 0.0899 g/l (14.4 times lighter than air), so it tends to dissolve very quickly [73], and can diffuse through materials that are impermeable to other gases.. All this makes it very difficult to detect any leakage [68].
At room temperature it is typically not very reactive due to the high stability of the molecules of H_2 that constitute it.

Among all fuels, the molecular hydrogen has the highest energy content per unit of mass (1 kg of H_2 contains the same energy of 2.1 kg of natural gas or 2.8 kg of gasoline), as can be deduced by Figure 2-1.



Fuel	LHV (MJ/kg)	HHV (MJ/kg)	Stoichiometric Air/Fuel Ratio (kg)	Combustible Range (%)	Flame Temperature (°C)	Min. Ignition Energy (MJ)	AutoIgnition Temperature (°C)
Methane	50.0	55.5	17.2	5–15	1914	0.30	540–630
Propane	45.6	50.3	15.6	2.1–9.5	1925	0.30	450
Octane	47.9	15.1	0.31	0.95–6.0	1980	0.26	415
Methanol	18.0	22.7	6.5	6.7–36.0	1870	0.14	460
Hydrogen	119.9	141.6	34.3	4.0–75.0	2207	0.017	585
Gasoline	44.5	47.3	14.6	1.3–7.1	2307	0.29	260–460
Diesel	42.5	44.8	14.5	0.6–5.5	2327		180–320

Figure 2-1: Hydrogen compared to other fuel in terms of Energy Content [74]

The only product of the reaction of hydrogen with oxygen is water, and even its combustion in engines and gas turbines produces small quantities of emissions. The NOx emissions increase exponentially with the rise of combustion temperature, but this can be controlled with proper temperature regulation [75].

2.1.2 Safety

Hydrogen diffuses through air much more rapidly than other gaseous fuels. It is easily permeable due to its low density and viscosity, which implies the risk of leakage from the circuits.
With a diffusion coefficient in air of 0.61 cm^2/s, the rapid dispersion rate of hydrogen is its greatest safety asset.

It is imperceptible to the human senses; even its flame has a low visibility.
Furthermore its flame is very hot (2207°C) and has a great velocity: 1.85 m/s, much faster than other fuels, such as gasoline vapor (0.42 m/s) or methane (0.38 m/s)[34].

The limit of flammability of hydrogen in air at ambient condition is 4–75%, much larger than methane (in air is 4.3–15 vol%) and gasoline (1.4–7.6 vol%) [34]. If released in confined, poorly ventilated rooms, it can cause detonations [76].
Being lighter than air, it tends to stratify at the top of a room, where, however, there may be dangerous ignition sources (lamps, electrical connections, etc.).

It must be carefully assessed also the danger of asphyxia, due to the replacement of the oxygen of the air.

Schematically, the types of risks related to hydrogen are three:
- Physiological: frostbite, suffocation, difficulty breathing;
- Physical: it causes embrittlement of normally ductile metals;
- Chemical: ignition, fire, explosion.

At room temperature, the hydrogen is chemically unreactive due to the high stability of the H_2 molecules that constitute it, indeed very high temperatures are needed to dissociate molecular hydrogen into atomic hydrogen. For example, even at 5000 K, about 5% of the hydrogen remains undissociated [34].

There are still many concerns about the safety aspects because of unfamiliarity with this energy carrier. However, a closer analysis resizes the concept of hydrogen dangerousness. Being the lightest element it is diluted and is dispersed very quickly in open spaces.

Furthermore, when it burns, hydrogen is consumed very quickly, always with flames directed upward, so flames from hydrogen have little chance to propagate to neighboring materials. This, combined with the brief duration of fire, reduces also the danger of toxic emissions.

Hydrogen, unlike fossil fuels, is not toxic nor corrosive and any losses from the tanks do not cause pollution problems of soil or groundwater aquifers.

Hydrogen has been produced and handled for several decades and the technology and regulations of safe storage and transportation of this substance are available. According to [77], it does not present additional risks compared with other liquid or gas fuels.

2.2 Production methods overview

Since hydrogen is not only the most widespread element but also the lighter, it is extremely volatile and so it is almost not present on Earth in the form of H_2.
It can be found in compound form: water and hydrocarbons mainly. It will need to be extracted from these, at the price of a given energy expenditure.

A variety of process technologies can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical.
A scheme of the most important different processes currently available for hydrogen production is presented in Figure 2-2.
Firstly, there are two major categories of sources from which to produce hydrogen: fossil and renewable.

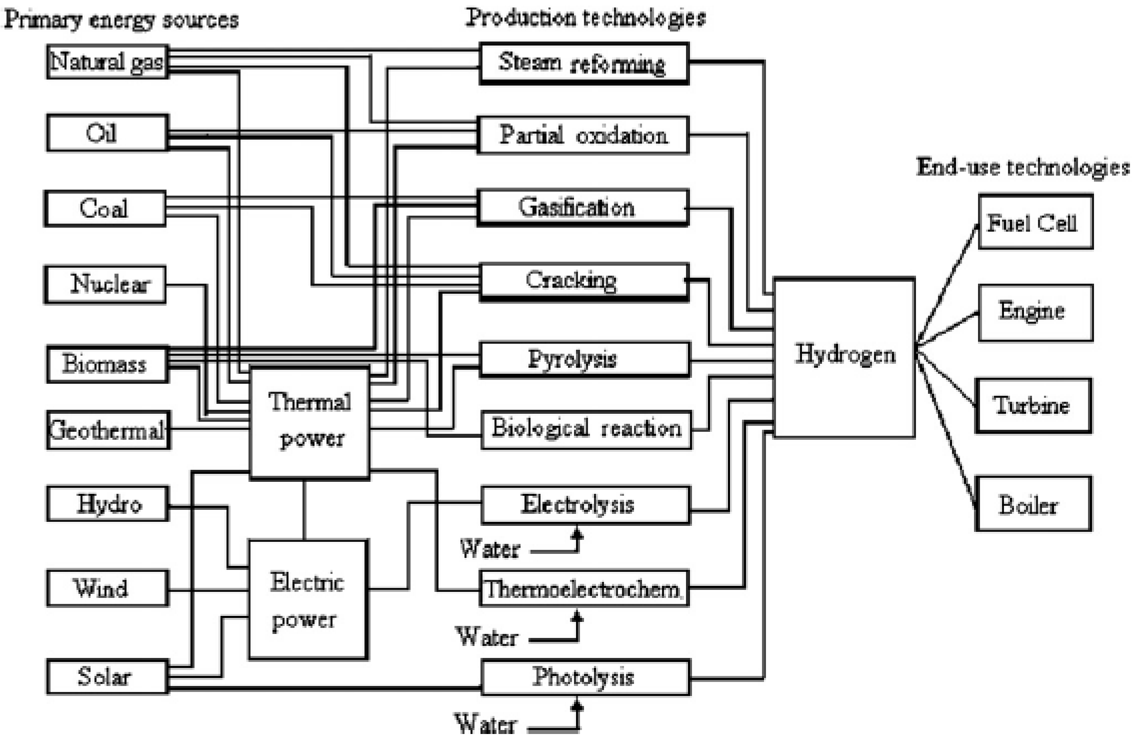


Figure 2-2: The main alternative methods of hydrogen production from energy sources.[27]

As can be seen in Figure 2-3, hydrocarbons (petroleum, natural gas) are actually the main source for the production of hydrogen, even though the water is the most abundant available source of hydrogen.
With the utilization of an external energy source, hydrogen can be produced from either fossil hydrocarbons or water alone, or from a mixture of both.
Anyway, since the energy demand of the process using hydrocarbons is much lower than that of water electrolysis, methods based on fossil hydrocarbons are preferred [27].

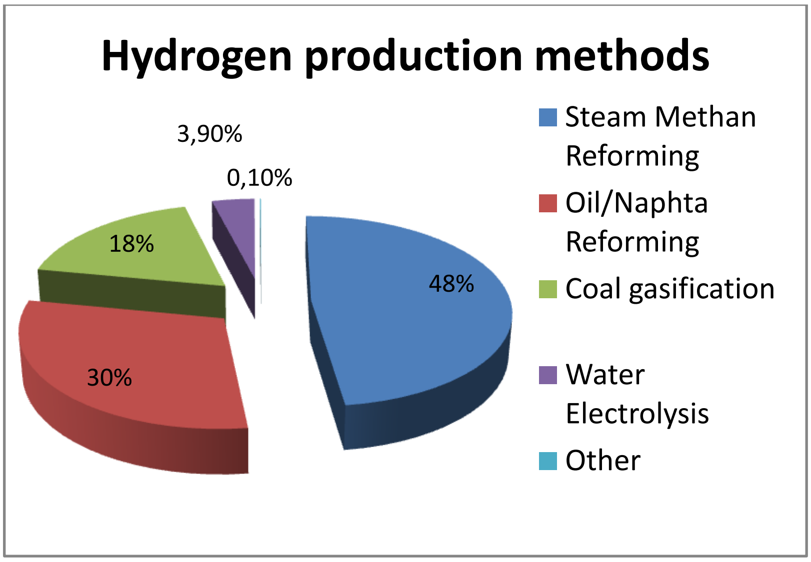


Figure 2-3: Hydrogen production methods breakdown. Adapted from [27]

Hydrogen can also be produced with a great variety of other methods (thermolysis, radiolysis, thermochemical cycles, photolysis et al.), but most of them have already been proved not to be economical, others are currently not ready for industrial application [78].

In the following paragraphs the main characteristics of the two most economical methods of hydrogen production (Steam Reforming and Coal Gasification, both from Fossil sources) are presented. Then, after a brief list of the principal methods from Non-fossil sources, it is made a comparison between all the commercially available technologies.
Then, the Water Electrolysis, the High Temperature Steam Electrolysis and the Sulfur Iodine thermochemical cycle (the three technologies on which this thesis study perform a techno-economic analysis) are described more in detail.

2.2.1 From fossil sources

2.2.1.1 Steam Reforming

Steam Reforming of hydrocarbons is the most efficient and economical process for the production of hydrogen, and it is considered particularly advantageous in large scale hydrogen plants [79].

Hydrocarbons react with steam in an endothermic reaction to form carbon monoxide and hydrogen. The most used raw material for the catalytic steam reforming process is natural gas. Other raw materials (propane, butane, et al.) can also be used, and the choice is usually dependent on the price and the readiness of raw material.
Three steps essentially constitute this process [80]:

i. Synthesis gas generation: $CH_4 + H_2O \rightarrow CO + 3H_2$
ii. Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$

iii. Gas purification

The steam reforming reaction is endothermic, and whereas the water-gas shift is slightly exothermic, the process is globally endothermic. So it is promoted at high temperatures. Furthermore, the process is characterized by an increase in the number of moles and is much favored for low pressure [80].
To achieve a complete conversion at 1 bar it is necessary a 900 °C temperature. If the pressure is increased, to achieve the same degree of conversion, an higher temperature is required. However, despite the increase of pressure is thermodynamically disadvantageous, it is carried out for two reasons: to reduce the volumes of the equipment and to produce hydrogen directly at high pressure in order to avoid a very expensive compression section.
Usually the trade off between technical and economic is around 30 bar.

Since the reactor operates at high pressures, and being unable to raise the temperature above 900 °C because of problems of strength of materials, values of H_2O/CH_4 ratio of 2.5—6 are used, to maintain good conversion values [80].
The reactor in which the process is realized it is a catalytic reactor (Nickel over basic Alumina).
It is essential to ensure a sufficient permanence time and an adequate surface/volume ratio, to perform a good heat exchange.
The catalyst used is very sensitive to sulfur compounds (sulfur is the main catalyst poison in steam reforming plants), so the raw material is desulfurized, in order to preserve the catalyst, before entering the reactor [70].
Then it is combined with the steam, and reacts over a nickel catalyst.

The typical yields of synthesis gas outlet are: H_2 74%, CO 18%, CO_2 6%, CH_4 2% [80].
After the reformer, the gas mixture passes through a heat recovery (and is cooled until 350 °C) and then to a water-gas shift reactor to produce extra hydrogen.
Efficiency of the steam reforming, defined as the ratio of hydrogen LHV to the energy input of raw material ranges between 65--75% [80].

Centralised fossil fuel-based production of hydrogen, could be the technology of choice in the medium to long term, only if combined with the capture and storage of CO_2. However, the capture and storage of CO_2 is not yet commercially proven [37]. Further R&D on the processes of absorption and separation are required.

2.2.1.2 From Coal Gasification

Coal gasification is a process by which the solid fuel reacts with oxygen and water, and it is transformed in gaseous products (syngas), rich on CO and H_2.
When the coal is heated up in a room with oxygene of > 95% purity, at high temperatures and elevated pressures, hydrogen-rich gas mixtures are produced [80].

Following the gasification process several other purification processes are necessary, in order to provide the user a current that meets the required standards.
The coal gasification is complex, because of the need of solid fuel handling including transport, size reduction and removing large amounts of ash. The solids handling operations significantly affect the cost of hydrogen production [80].
However, the production from any fossil fuel, as well as contribute to exhaustion of fossil reserves (while the ultimate aim of hydrogen is just to free ourselves from this dependence), it causes CO_2 emissions.

2.2.2 From Non-fossil sources

2.2.2.1 Hydrolysis

The hydrolysis is a chemical reaction that consists in the splitting of the water molecule to produce hydrogen and oxygen. Whatever process is chosen, it requires energy to be realized. There are several technologies that can be used to accomplish the hydrolysis of water: electrolysis, thermal hydrolysis or thermolysis, thermochemical hydrolysis, photolysis and radiolysis [80]. In the following paragraphs the most relevant of these technologies will be briefly described.

The electrolysis of water consists in the breaking of the water molecule itself by means of the passage of electric current in an electrolyte to obtain hydrogen and oxygen, which develop into gaseous form, and are collected [30].

It can indicate the year 1800 as a start date of actual scientific observations in relation to the electrolysis of water. The experimenters Nicholson and Carlisle, using as source of direct current, built a simple electrolysis cell, by means of which the evidence of the decomposition of water into hydrogen and oxygen was given [81]. The construction of the first commercial facilities began in the first years of the last century. The most development occurred in the decade 1930-40, especially with the exploitation of sources of hydroelectric power. Anyway in the 1960s, the industrial production of hydrogen shifted slowly towards a fossil-based feedstock.

2.2.2.2 Thermolysis

Theoretically the simplest method to separate water would be the direct thermal dissociation. It consists in the breaking of the water molecule at high temperature through simple heating until temperatures greater than 2000 °C [30]. The present compounds after the thermolysis reaction are: H_2O, H_2, O_2, H, O and OH [80]. The thermolysis product of water is a mixture of different gases; the equilibrium composition depends on pressure and temperature of the reaction. Appreciable quantities of H_2 can only be obtained significantly above 2000 °C: in fact the degree of water dissociation at 2000 °C is only 1%; more than

3000 °C are required to achieve a 50% of separation [80], and over 5000°C for a complete separation [30].

The main problems are related to the materials needed at extremely high temperatures [80]. Also the subsequent need for separation of molecular hydrogen from other compounds is difficult to manage: the low temperature removal requires a very rapid cooling (2000 K in a few milliseconds!); while the separation at high temperature could be made through microporous ceramic membranes, metallic membranes, or centrifugation. Another phenomenon has to be taken into account: the recombination of products at high temperature. All this makes an economic utilization very difficult.

2.2.2.3 Thermochemical hydrolysis

Incorporation of chemical reactions to the decomposition process can significantly lower the temperature threshold of the heat to be required [30].
In thermochemical water splitting, also called thermolysis, heat alone is used to decompose water to hydrogen and oxygen [82].

The thermochemical hydrolysis is the use of heat at high temperatures in presence of a chemical catalyst to decompose water, obtaining hydrogen and oxygen, without involving electricity use.

A thermochemical process consists of several chemical reactions with the net products of these reactions to be hydrogen and oxygen. This implies that the water is the sole feedstock to the process and all other reactants can be recovered and reused within the process [30].

Therefore chemical reagents have been proposed to lower the temperatures. Research in this area was prominent from the 1960s through the early 1980s [83]. However, essentially all R&D stopped after the mid-1980s, until recently [29]. There are more than 300 water splitting cycles referenced in the literature [84] [85].

The list in Figure 2-4 [30] contain the processes regarded as the most relevant, with temperatures mainly comprised between 600 and 1,000 °C. These temperatures can be obtained by solar heaters and NPPs as heat sources; furthermore in current chemical plants can be found materials capable to resist at the above mentioned temperatures [30].

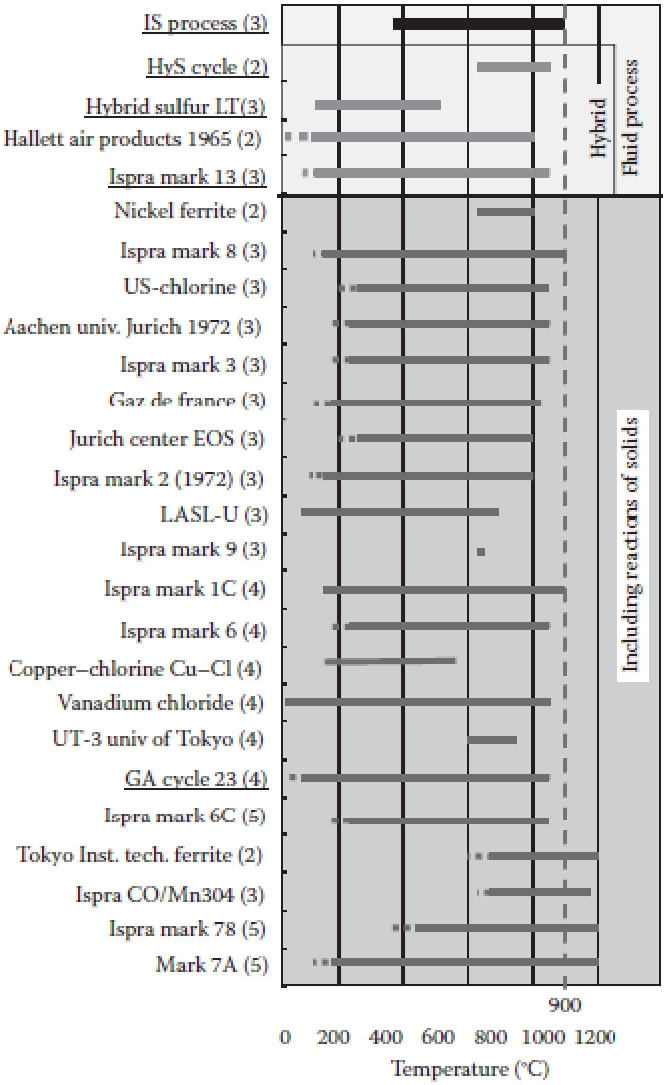


Figure 2-4: Selected major thermochemical processes of hydrogen production. Adapted from[30]

Thermochemical cycles consist in multistep processes where water is decomposed in hydrogen and oxygen via two or more chemical reactions that form a closed cycle.

Norbeck explains that in choosing the process there are five criteria which should be met [82]:

1. Within the temperatures considered, the ΔG of the individual reactions must approach zero. This is the most important criterion;
2. The number of steps should be minimal;
3. Each individual step must have both fast reaction rates and rates which are similar to the other steps in the process;
4. The reaction products cannot result in chemical-by-products, and any separation of the reaction products must be minimal in terms of cost and energy consumption;
5. Intermediate products must be easily handled.

The U.S. DOE has active projects investigating several of these processes focused on improving materials, lowering cost, and increasing efficiency [84]

Research by Schultz identified 115 different thermochemical cycles. The sulfure iodine (SI) process proved to have the highest efficiency [86].

2.2.2.4 Radiolysis

Water can also be split by high-energy radiation. This phenomenon is very well known in the (nuclear) Water Reactors, where the irradiation causes a variation of H_2 an H^+ concentration in the reactor pool.
The overall reaction of water radiolysis is [80]:

$$H_2O \rightarrow aH + bOH + CH_2 + dH_2O_2 + eOH_{aq}^{-} + gH_{aq}^{+}$$

Energy from nuclear sources is in the form of high energy photons, γ-rays, high-speed either charged particles (α or β radiation) or uncharged neutrons.
The rate of Energy transfer to the medium is called linear Energy transfer (LET). The radiochemical yield, G value, is defined as the number of molecules converted per 100 eV absorbed energy, depends on the LET value of the radiation [87].
The G value of H_2 is greatly affected by the chemical state of the medium: the irradiation of water in the liquid state with gamma rays using Co-60, gives a G(H_2) of 0.45, while in the vapourstate at 100°C is 5.2. With Po-210 a G(H_2) of 1.8 can be obtained [80].

2.2.2.5 Photoelectrolysis

Finally, the Photoelectrolysis of water is the process whereby light (a photon) is used to split water directly into hydrogen and oxygen.
The key challenge is to develop photo-electrode materials and their processing technologies with high-efficiency (performance) and corrosion-resistance (longevity) characteristics [80].

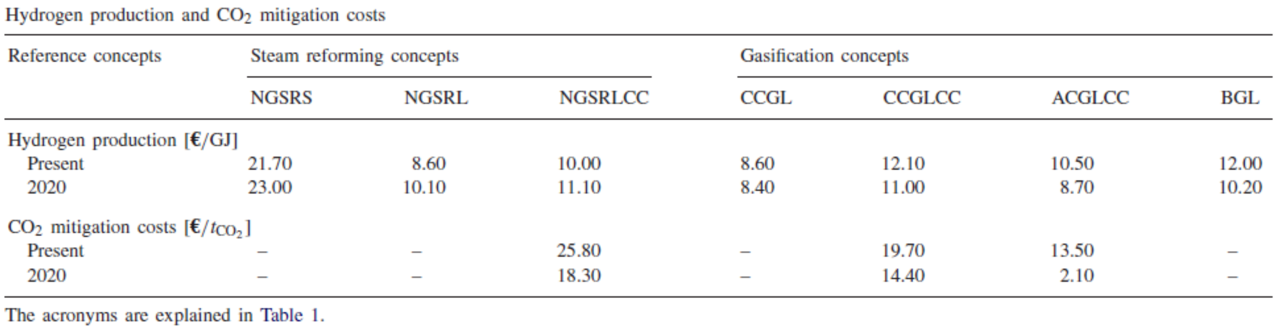
2.2.3 Comparison between different production techniques

Among the various methods to extract hydrogen from water, electrolysis is currently the only one that has a commercial relevance [34], [37].
Currently only a small part (4%) of the hydrogen for industrial applications required by the market is produced by electrolysis [68]. In fact, for large scale installations, electrolysis presents a higher capital cost, and with regard to the variable costs, especially the cost of the electricity is very heavy, compared to production from fossil fuel [37] (Steam Methane Reforming, for instance), where the fuel cost is maintained very low by the current price of Natural Gas.

Nowadays Steam-methane reforming is the most common method of producing hydrogen in the U.S. It requires combustion of roughly 10-15% of the methane in the feed stream to generate the heat and steam necessary to split the remainder of the methane; consequently, the resulting emission of CO2 is a concern [46].

Furthermore the electrolysis guarantees a purity level that is not reached by the other techniques. In fact in the gasification, steam reforming or partial oxidation traces of CO are present inside the hydrogen flow: this makes necessary the realization of massive sections of purification (very expensive)[78].

A cost comparison between different methods of hydrogen production has been made by [37]:



Hydrogen production and CO_2 mitigation costs

Reference concepts	Steam reforming concepts			Gasification concepts			
	NGSRS	NGSRL	NGSRLCC	CCGL	CCGLCC	ACGLCC	BGL
Hydrogen production [€/GJ]							
Present	21.70	8.60	10.00	8.60	12.10	10.50	12.00
2020	23.00	10.10	11.10	8.40	11.00	8.70	10.20
CO_2 mitigation costs [€/t_{CO_2}]							
Present	–	–	25.80	–	19.70	13.50	–
2020	–	–	18.30	–	14.40	2.10	–

The acronyms are explained in Table 1.

Figure 2-5: : Cost comparison of different hydrogen production methods [37]

In a more recent study, Guerrero Lemus [28] makes a cost comparison between the main hydrogen production technologies from fossil sources, as we can see in Figure 2-6.

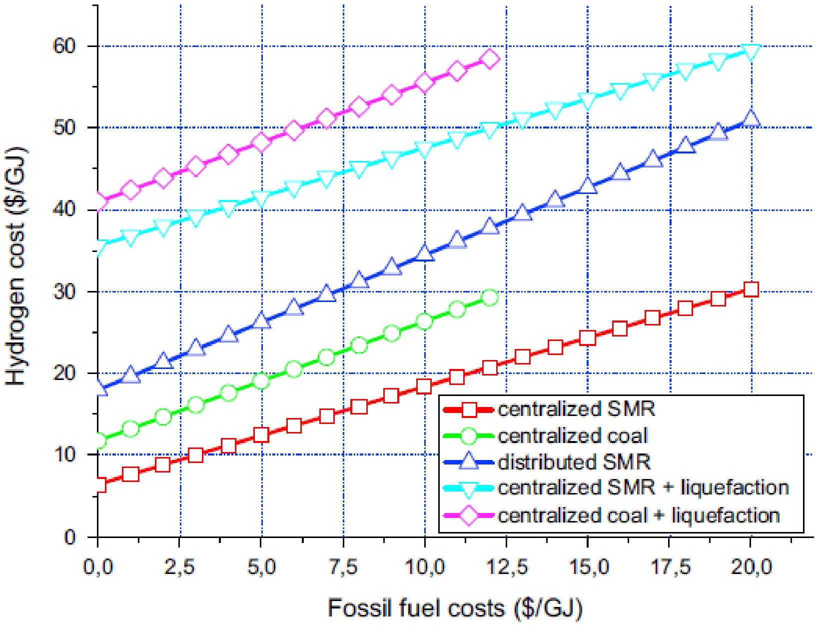
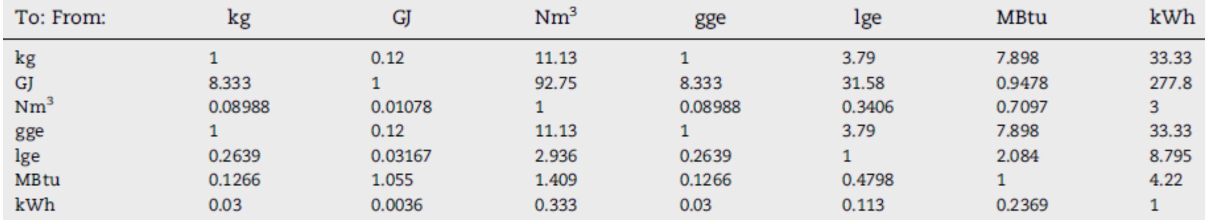


Figure 2-6: Linear dependences of natural gas and coal prices to centralized and distributed SMR and coal based hydrogen costs [28]

It is clearly visible how Steam Methane Reforming is the cheaper technology for any cost of the fuel.

The cost of Natural Gas during this year varied between 2.44 and 4.54 $/MMBtu [88] (= 2.58 – 4.79 $/GJ), so the centralized Steam Methane Reforming (defined SMR in Figure 2-6**Errore. L'origine riferimento non è stata trovata.**) cost, that is taken as a comparison parameter, varies reasonably between 10 and 13 \$/GJ, which roughly means (according to the GJ/Nm^3 conversion, from Figure 2-7) 0.10—0.13 €/Nm^3.



To: From:	kg	GJ	Nm^3	gge	lge	MBtu	kWh
kg	1	0.12	11.13	1	3.79	7.898	33.33
GJ	8.333	1	92.75	8.333	31.58	0.9478	277.8
Nm^3	0.08988	0.01078	1	0.08988	0.3406	0.7097	3
gge	1	0.12	11.13	1	3.79	7.898	33.33
lge	0.2639	0.03167	2.936	0.2639	1	2.084	8.795
MBtu	0.1266	1.055	1.409	0.1266	0.4798	1	4.22
kWh	0.03	0.0036	0.333	0.03	0.113	0.2369	1

Figure 2-7: Conversion factors for current hydrogen units

However, also the CO_2 emissions should be taken into account.

As observed in Figure 2-8, the emissions related to coal gasification and SMR are about one order of magnitude higher than those corresponding to renewable energies, and nuclear electrolysis in particular.

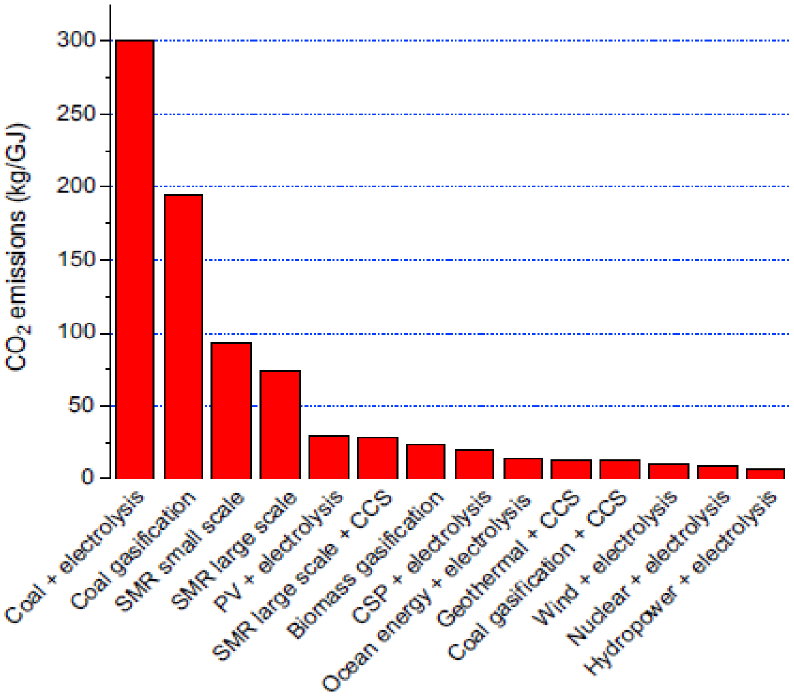


Figure 2-8: Comparison of CO2 emissions for different technologies [70]

Starting from these emissions data, [79] states that if an emission carbon tax of 50 \$/$TmCO_2$ is added to coal gasification, then nuclear hydrogen would be very close to parity at present, while for the Steam Methane Reforming the parities could be achieved within some years, if the WE reach the cost target proposed by IEA in [89].

Bartesls observes that a kilogram of hydrogen has the approximate energy content of one gallon of gasoline; therefore the cost of hydrogen per kilogram is directly comparable to the gasoline cost per gallon. Since the cost of gasoline ranges within 2.00e4.00 \$/gal [90], 4 \$/kg (roughly 0.35 €/Nm^3) can be considered the superior limit for an economically acceptable hydrogen production.

As for the non-fossil sources, according to [90] they have higher H_2 production costs: for instance, Electrolysis by nuclear energy (from LWR) presents extimated costs between 4.36 and 7.36 $/kg.
Anyway, processes as thermochemical water splitting (coupled with VHTGR) are considered prosiming from the economical point of view: a cost of 1.84 $/kg could be achieved [90].

Of course the cost of the electrolysis depends on the cost of electricity and consequently the energy source with which the electric energy is obtained has a crucial role in the evaluation of water electrolysis economic profitability.
Electrolysis is already considered the best choice for small-scale and decentralized productions, like the coupling with wind power plants [91].
The question is if it can be affordable even for large-scale production.

Taking 12 c€/Nm^3 [79] as cost of hydrogen from Steam Methane Reforming, and considering an (optimistic) efficiency of ≈4 kWh/Nm^3 [69], it would take an EP of 3 c€/kWh just for the electrical costs not to be superior to the total Reforming costs. Clearly also the CAPEX and the non-electric OPEX must be taken into account, so in near future it seems really difficult for the hydrogen from Water Electrolysis to be cheaper than hydrogen from Steam Methane Reforming, at least without considering a much heavier tax on CO_2 emission.
Thus, the aim of this thesis project is not to verify if hydrogen from WE costs more than the one from fossil sources, but to understand if it is possible to deploy a large-scale plant, which works in the Load Following mode, and produces hydrogen (without involving CO_2 emissions) at a reasonably low price.

2.2.4 Alkaline Water Electrolysis (AWE)

2.2.4.1 PEM and Alkaline Water Electrolyser

The water electrolysis consists in the decomposition of water molecules, under electric field generated between two electrodes immersed in a medium electrolyte, by mean of the passage of an electric current. The process occurs in installations commonly called electrolyzers. This paragraph describes: the operating principle of an electrolyzer, the thermodynamics of the process, the materials and the main organs that compose it, the possible modular configurations (series and parallel), the two technologies of commercial use (alkaline and PEM) and it presents the current market of electrolyzers.

The electrolyzers are composed of a few simple parts and require little space. The basic parts of the cell are the container of the liquid to be subjected to electrolysis, the electrodes, consisting of two metal surfaces arranged facing each other (between which a direct current source, external to the cell, maintains a sufficient potential difference) and the diaphragm, which separates the cell into two compartments, anodic and cathodic, where the two semi-reactions (reduction and oxidation) take place, spatially separated [92].

When the switch of the electric power supply circuit is turned on, the electrolysis process starts: gas bubbles of different nature are formed on the surfaces of the two electrodes, and migrate to the surface of the liquid, above which they can be collected separately, thanks to the presence of a diaphragm. Its role is fundamental, because it prevents the mixing, allowing only one type of ions (negative or positive, depending on the nature of diaphragm), to pass through it [92].

The passage of electrical current in the cell, indeed, creates an electric field over the electrolyte which forces the negative ions (anions) to move towards the anode (positive pole) and positive ions (cations) to the cathode (negative pole).

In Figure 2-9 a schematic representation of an Alkaline EZ cell, where the electrolyte is a solution of potassium hydroxide (KOH), and the electric charge is brought by the electrons in the upper part of the circuit (electric part), and by the OH^- ions in the lower part of the circuit (electrolytic part). OH^- ions are generated at the cathode, then they migrate under the driving force of the electric field (difference of potential between the two electrodes), pass through the diaphragm, and are consumed at the anode.

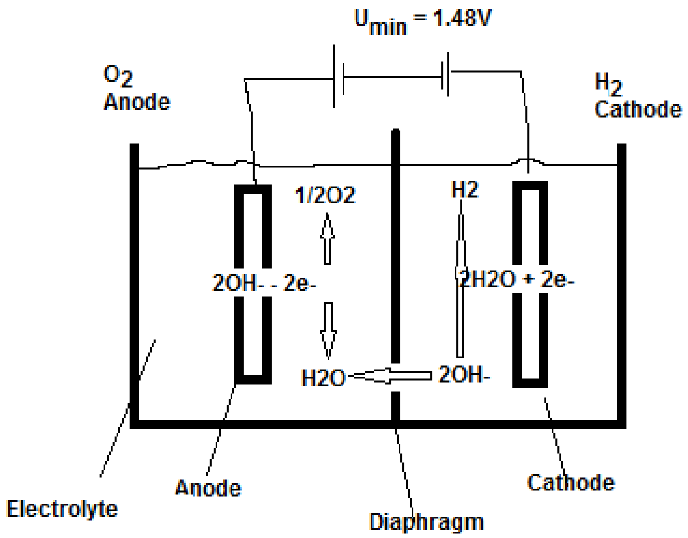


Figure 2-9: : Alkaline Electrolyser Cell reactions scheme [92]

At the same time the ions already present around the electrodes react:

- by absorbing electrons from the metallic circuit and reducing themselves at the cathode;
- by yielding electrons to the circuit and oxidizing, at the anode.

Hydrogen and oxygen are obtained separated since they develop each one in correspondence of one of the two electrodes. The salts or alkali that must be added to the water to increase the conductivity are not consumed, so the only substance that is consumed is water.

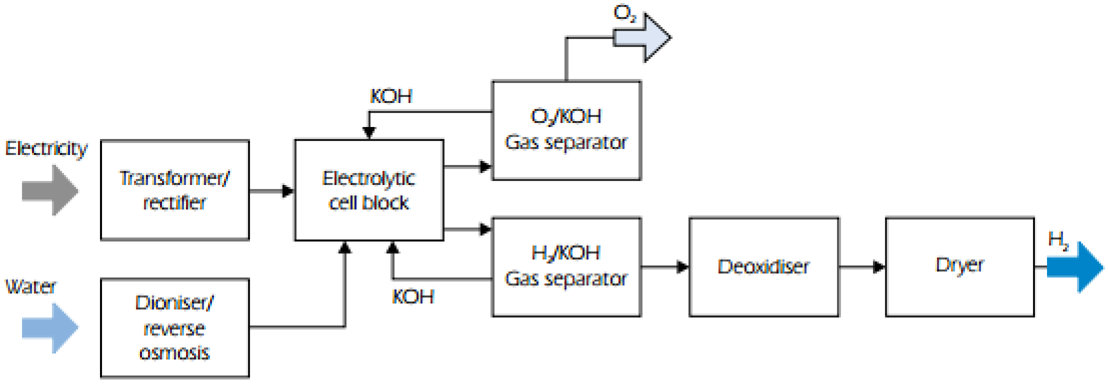


Figure 2-10: Process diagram of alkaline electrolysis [50]

2.2.4.2 Electrolyser components

THE ELECTROLYTE

It is well known that pure water contains ions (H^+ and OH^-), formed by self-dissociation water.
At constant temperature the concentrations of both the species are constant and equal to each other. This concentration is very small and particularly at 25 °C avails 10^{-7} mol/l.
With a very low concentration of ions electric current passing through the water would be not sufficient, so it is necessary to use a trick to overcome the problem. A substance that increases the electrical conductivity without playing any role in the electrode reactions, is added to the water [92].
Strong acids or alkalis, for example, carry a considerable enrichment H^+ and OH^- ions, promoting the conductive mechanism.
Alkali such as NaOH or KOH in a concentration (around 25-30% [93]) that gives to the electrolyte the maximum conductivity are the ones used in practise.
In Particular, the first one has a lower conductivity than the second, but it is more economical. These substances allow the use of construction materials with good resistance to corrosion and easily available such as carbon steel, stainless steels and nickel [92].
Since KOH combines with CO_2 to produce potassium carbonate, it is necessary a periodic replenishment in those cells that operate at atmospheric pressure and are in contact with the external environment. Obviously the alternative is the use of hermetic cells that do not have this loss. Very pure water is fundamental, to avoid the production of chlorides and sulphates that would otherwise occur with a normal water flow; these last slowly attack and corrode the material of the electrodes.

THE ELECTRODES

The distance between the electrodes should be the minimum compatible with the construction requirements, as to reduce the resistance of the electrolyte to the passage of the current.

The transverse dimension of the cells has obviously constructive dimensional limitations.

The alkaline electrolytes are compatible with the steel, and in particular conventional constructions are made of nickel steel. The electrodes must withstand in bias conditions, which are more severe than a normal contact with the electrolyte, and must offer an overvoltage as low as possible both with respect to hydrogen and oxygen [92].

This involves a choice of appropriate materials respectively for the cathode and the anode.

The overvoltage can be further lowered by special surface treatments and deposition of electrocatalysts. The potassium hydroxide (KOH) and the electrodes of nickel stainless steel allow to obtain the best performance / cost compromise.

Fora an Alkaline electrolyte (KOH), the cathodic reactions are:

$$4H_2O \rightarrow 4O^{2-} + 8H^+$$
$$4O^{2-} + 8H^+ \rightarrow 4OH^- + 4H^+$$
$$4e + 4H^+ \rightarrow 2H_2$$

While, the anodic reaction is:

$$4OH^- \rightarrow O_2 + H_2O + 4e$$

The reaction at the anode is therefore an oxidation in which free electrons are deposited, while the reaction at the cathode is a reduction, in which the freed electrons, emitted from the anode are transferred to the H^+ ions.

Some observations are due [92]:

- in terms of volume, the hydrogen produced is twice the oxygen;
- an equal number of electrons is collected at the cathode and released at the anode, closing in a balanced way the electrical circuit within the cell;
- as soon as the ionic species are transformed into neutral molecules by interaction with the electrodes, the same number of ions is formed again. This is due the thermodynamic need to maintain steady the concentration of ions within the solution. The process then is continuous until the external electrical source provides electrons to the cathode, which it recover at the anode.

The electric charges, however, are not transported through the cell with a massive shift of the ions. The displacement of the electric charges is made by mean of the bonds created between the water molecules, with an apparent speed much higher than the one that would be permitted by the real mobility of the ions.

THE DIAPHRAGM

The cell is separated into the anodic and cathodic part by the diaphragm, which must have at the same time two fundamental properties: low resistance to the passage of electric current and gas impermeability. To meet the first parameter the diaphragm material must be porous, easily impregnated with electrolyte and thin. These factors may be in contrast with the need to keep well separated the hydrogen and the oxygen, avoiding mutual pollution, that could even result in the formation of explosive mixtures [92].

Obviously, the diaphragm must maintain adequate chemical and mechanical resistance under the electrolysis conditions. Materials such as asbestos fibers would meet well the role of separator, but because of their toxicity used artificial fibers or metal mesh are most often.

2.2.4.3 Cell Configuration

When requested by the capacity of the plant, two or more cells may be placed in parallel so that the total current fed (and therefore the obtained production) is a multiple of the one of a single cell [68].

This arrangement constitutes a monopolar system, since each electrode has a single polarity: it follows that the current generator has to provide a very low voltage, equal to that of a cell (eg. 2 V) and a relatively high current, equal to the sum of all the cell currents.

Alternatively, the cells can be connected in series: in this case the current supplied is the same for each cell and the total voltage applied is the sum of the individual cell voltages. From the electrical point of view this alternative is the best one. In this case the configuration is bipolar: each electrode acts as cathode on one face and as anode on the opposite one [68].

In the case of parallel connection (or monopolar), as shown in Figure 2-11, each anode is separately connected to the positive pole and each cathode is, in the same way, connected to the negative pole.

Each cell can thus be switched off individually (or removed to perform maintenance or replacement), keeping in operation the other; the voltage used for the parallel is the same as used for the single cell, but of course the current demand will be greater.

In the case of electrolyzers in series (or bipolar) each cell shares a electrode with the adjacent cell, as shown in Figure 2-11.

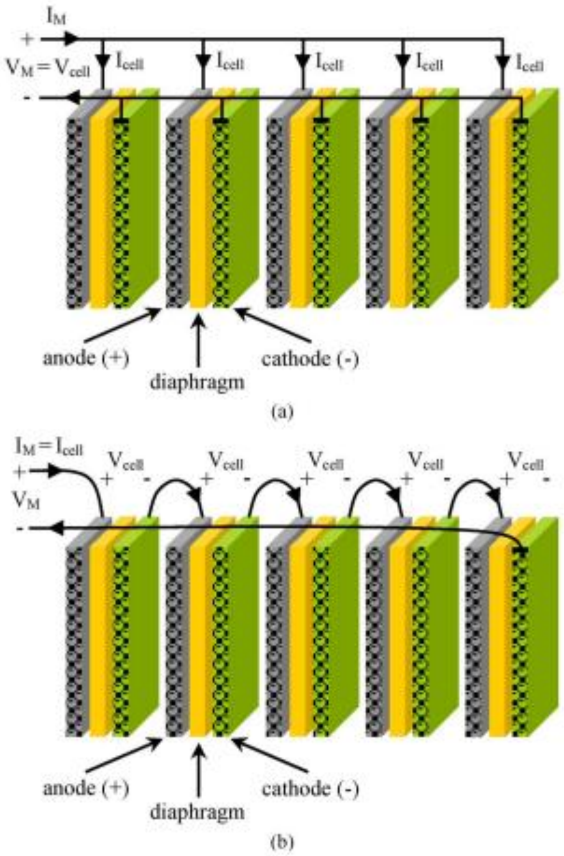


Figure 2-11: . Configuration of an electrolysis module: (a) unipolar or parallel configuration, and (b) bipolar or series configuration [94]

The current consumed by the series is the same used by the individual cell, while the request voltage of the series is a multiple of that of the single cell.

The advantages and disadvantages of a cell system in parallel with respect to one cell in series are summarized in the following table [92]:

Advantages	
Parallel	**Series**
Ease of construction	High current density
Simple structure	Low cell voltage
Ease of single cell control	High temperature and pressure
Absence of eddy current	Less required space
No pumps, filters, heat exchangers	Possibility of automatic control
High useful life (25 years)	All cells share the same electrolyte, allowing the free movement
Disadvantages	
Parallel	**Series**
Very spacious	Difficult realization
Impossibility of realization of a system with automatic control	Presence of eddy currents (reduction yield)
Only low pressure operation	Requires the presence of pumps, filters, exchangers
Requires large amounts of electrolyte	-
Ability to collect impurities and products due to corrosion inside the cell	-

Table 2-1: Series and Parallel Cell configuration advantages and disadvantages

2.2.4.4 Electrolysis Thermodynamics

The enthalpy of the overall reaction water separation at 25 ° C and atmospheric pressure (ΔH^0_{298K}) is a function of the difference of Entropy (ΔS^0_{298K}) and Gibbs Free Energy (ΔG^0_{298K}), according to the following relationship:

$$\Delta G^0_{298K} = \Delta H^0_{298K} - T * \Delta S^0_{298K}$$

Where [30]:

$$\Delta H^0_{298K} = 285.8 \frac{kJ}{mol} \;\; ; \;\; T * \Delta S^0_{298K} = 48.7 \frac{kJ}{mol} \;\; ; \;\; so \; \Delta G^0_{298K} = 237.4 \; kJ/mol$$

The electrical work required defines the minimum voltage at which the water can be electrochemically separated.

The voltage that has to be applied to provide *237.4 kJ/mol* at a temperature of 25 °C and pressure of 1 atm is:

$$V_{rev} = \frac{\Delta G^0_{298K}}{2F} = 1.23 \; V; \; \text{where } 2F = 2 * 96{,}500 \; C \; \cong 53.6 \; Ah$$

Clearly the ΔG, and the V_{rev}, vary with temperature and pressure.

This dependence of V_{rev} by thermodynamics (TD) conditions becomes very relevant in the High Temperature Electrolysis, treated in the following paragraph **Errore. L'origine riferimento non è stata trovata.**.

The water splitting is an endothermic chemical reaction, which requires a supply of heat to be able take place at constant temperature. This can be achieved in a simple way by utilizing the heat generated by the unavoidable ohmic resistances, that oppose the passage of the current. To achieve this aim it is sufficient to raise the cell voltage to a voltage value equal to 1.49 V, the so called 'thermoneutral' voltage.

If the voltage is inferior to this value, the temperature tends to decrease, if opposite it tends raise, and a system that removes the heat from the cell is necessary.

It is important to evaluate the energy expenditure required to perform electrolysis. Let us refer to a Nm^3, standard unit of volume of gas at standard conditions. The amount of electricity required to produce a Nm^3 of hydrogen can be simply evaluated as follows evaluated:

$$1[Nm^3] * \frac{1}{22.414}\left[\frac{kmol}{Nm^3}\right] * 53.6\left[\frac{Ah}{mol}\right] = 2{,}393\ [Ah]$$

Which, at the thermoneutral voltage, leads to an *ideal* specific electric energy of:

$$W_{id} = 2{,}393\ [Ah] * 1.49\ [V] = 3.56\ \left[\frac{kWh}{Nm^3}\right] = \ 39.91\ [\frac{kWh}{kg}]$$

However, as already pointed out, within the cell the cell voltage is necessarily greater than the thermoneutral value, and it is usual to indicate the cell efficiency as the ratio between the thermoneutral voltage and the real voltage.

As regards the large-size Alkaline Electrolyzers the value of the real voltage of the cell is around 1.7 to 1.9 V (with efficiency values of voltage comprised between 0.78 and 0.85) [92]. Thus the specific energy consumption is between 4.3 and 4.7 kWh per Nm3 of hydrogen produced.

2.2.4.5 Cell Voltage

The practice requires electrolysis to produce reasonable amounts of hydrogen per unit time. This introduces a number of additional dissipations, in support of productivity, which result in voltage drops through the various components of the cell.

They are primarily resistive losses related to the carriage of the current to the electrodes, and secondarily losses due to the passage of electric charges from the electrode surface to the liquid phase or vice versa and to the crossing of the electrolyte and diaphragm.

The real voltage of the cell is then given by the sum of [68]:

- Thermodynamics minimum voltage: V_{rev};
- Ohmic resistances: $\sum R_i$
- Overvoltage at the electrodes: μ_A and μ_C .

Over voltages are related to the speed of reactions that occur on the electrodes and are a function of current density as well as of the nature of the electrode itself.
The approximate value of over potentials is described by Tafel equation [68]:

$$\mu = C_1 + C_2 * \ln(i)$$

where i is the current density.
The ohmic resistance is approximately linear with the current density.

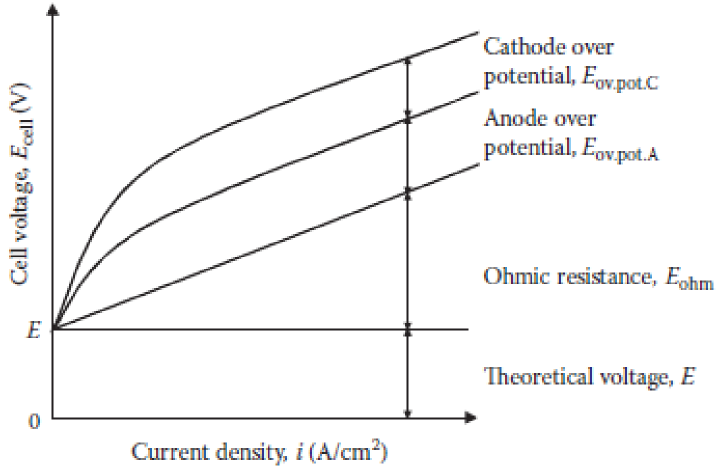


Figure 2-12: Cell voltage breakdown [68]

The anode and on the cathode are usually deposited special "activators" or "electro-catalysts", in order to minimize the over voltages, which being kinetic factors depend strongly on the temperature at which they operate.
Modern systems minimize this problem operating at rather high temperatures, around 90°C, that is the limit imposed by the material of construction of the separation membrane.
Even though the ohmic resistance between inside the electrolyte contributes less than the over voltages, it is not negligible.
The ability of the designer is to minimize the internal resistances, selecting in a suitable way the electrolyte, the diaphragm, the configuration of cells, the construction materials and the surface treatments of the electrodes.

2.2.4.6 Operating Parameters

The most relevant operational parameters are: temperature, pressure and current density.

As for the temperature, it is common practice to operate at the highest possible temperature, compatibly with the used materials.
Generally, the diaphragm is the most vulnerable component of the system and therefore the evaluation of the temperature is closely linked to the type of the diaphragm [92].

As for the pressure, its increase has a beneficial effect for the performance, but it is technologically complex, due to the difficulty to maintain separate streams of hydrogen and oxygen, avoiding leakage. Most of the commercial electrolyzers operates at atmospheric pressure, sufficient condition to collect the produced gases in watertight gazometers. The disadvantage of this technology is that it therefore requires the presence of a compression section of the downstream gas, to provide hydrogen to the required pressure (in order to store or transport it) [92].

Alternatively, advanced electrolyzers operate directly at high pressures.

It has to be underlined that the compression work performed *before* the electrolysis (which means that the object of the compression is the liquid) leads to an energy consumption quite negligible compared to the demand of mechanical compressors of gas. The high pressure also reduces the specific volume of the gas and then the volume of the vessels and the pipes.

The amount of decomposed water per unit of time, that is, the productivity of the electrolyzer, is determined by the current density that flows through the system and the number of cells crossed. The relationship between the current density and the area of a single electrode determines the operational average current density. Increasing current density increases the resistive losses and simultaneously decreases the size of the electrodes and the cells, and consequently also their costs. At the design stage a compromise has to be found, choosing a value of current density that minimizes the total cost (operating costs and depreciation). Typical values of the current densities are included between 100 and 300 mA/cm^2 [95] for conventional plant, and can reach 400 mA/cm^2 and for more advanced systems.

2.2.4.7 Current Electrolysers Market

There are several technologies that realize the electrolysis of water, which differ in the level of pressure, and type of electrolyte adopted.

As regards the pressure level there are two techniques: the first consists in producing hydrogen at ambient pressure, which is subsequently compressed up to the required pressure by a gas compressor; the second is to produce it directly in pressure. It is also possible to perform electrolysis using an alkaline electrolyte or a chemically reactive membrane (PEM, Polymeric Electrolyte Membrane).

2.2.4.7.1 High Pressure vs Low Pressure Electrolysers

As regards the high-pressure electrolysis the main advantages are the lower energy absorption and lower the cell size. The disadvantages are: higher cost of sealed containers under pressure, greater difficulty in maintaining the separation between hydrogen and oxygen, and greater amount of dissolved gas in the electrolyte [92].

On the other hand the electrolysis low pressure has advantages in terms of ease of construction and of purity of the hydrogen stream produced, but has the great disadvantage of the installation that requires an expensive compressor downstream of the process, bringing the produced hydrogen to the operating pressure of the user[29]. In fact, most of the uses of hydrogen requires it to be compressed to a quite high pressure. Consequently the cost of hydrogen production increases because of the presence of the compressor, which is generally characterized by high costs, costly and frequent maintenance, and low reliability.

2.2.4.7.2 Alkaline vs PEM Electrolysers

As can be seen in the Figure 2-13, the basic principle of AWE and PEM WE is the same. The main difference is represented by the electrolyte material, and so by the ion that is allowed to pass through it. We have already seen that in the AWE the OH^- ions move from the cathode to the anode, and are consumed there; on the other hand, in the PEM WE the polymeric membrane consents the passage only to H^+ ions, so they move from the anode to the cathode.

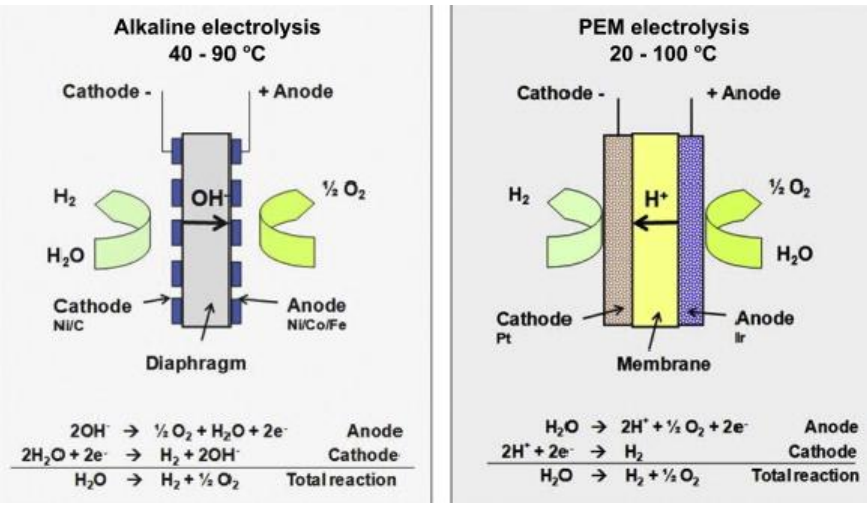


Figure 2-13: AWE vs PEM WE. Basic scheme and anodic and cathodic reactions [52]

On average the cell voltage of an AEZ arises between 1.8 and 1.9 V, while for a PEM it can be up to 2.1 V. Therefore, the AEZ has lower power consumption and also features the best overall returns. Furthermore, the AEZs have much more hours of operating experience on a commercial scale than PEM ones [92].

Currently on the market there are mostly alkaline electrolysers (especially for the large scale EZs), with rare exceptions. In fact, the first technology is that most proven, crucial aspect in an industrial context.

The PEM electrolysis is considered to be a promising method because it is able to operate at high current densities due to an extreme volume reduction when compared with the alkaline water electrolysis [96].

An interesting aspect regarding the PEM technology is the following: PEM cells, such as fuel cells based on similar technology, use noble metals (Pd, Pt), elements of which the Earth is very poor. Therefore, when these cells were to assume an important role it would be essential to find the precious metals or find alternatives.

2.2.4.7.3 High Temperature vs Low Temperture Electrolysis

As previously seen, at 25 °C and 1 atm, the minimum voltage needed to split the water is 1.23 V. However, this voltage value decreases as the temperature increases of about 0.4 to 0.5 mV/°C [92]. Indeed, as the temperature increases the resistivity of the electrolyte and overvoltages electrode decreases, reducing the dissipation of energy. It is therefore appropriate to operate at high temperatures, compatible with the materials used, in order to realize the electrolysis at a lower voltage, increasing the efficiency of the process.

Figure 2-14 shows the dependence between the voltages and reversible thermoneutral temperature of the electrolyte. There are three main areas enclosed by two lines.

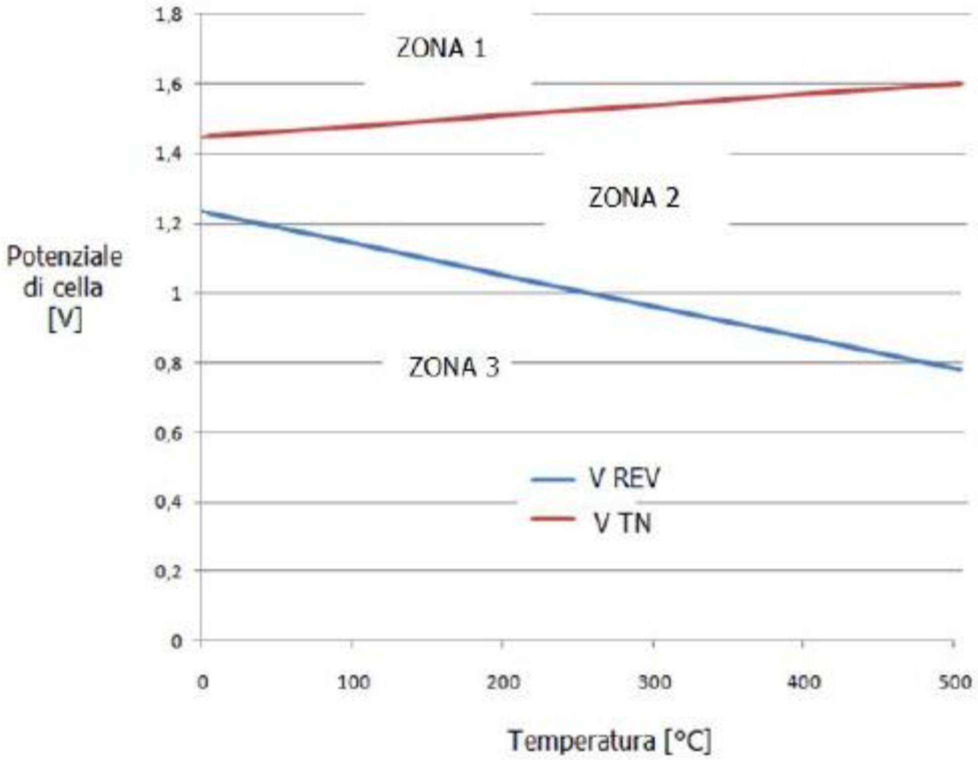


Figure 2-14: Vatiation of the Thermoneutral voltage (red) and Reversible voltage (blue) according to the operating temperature [92]

When the voltage is between the upper and lower limits (Zone 2) the electrolysis process absorb heat, to take place at constant temperature.

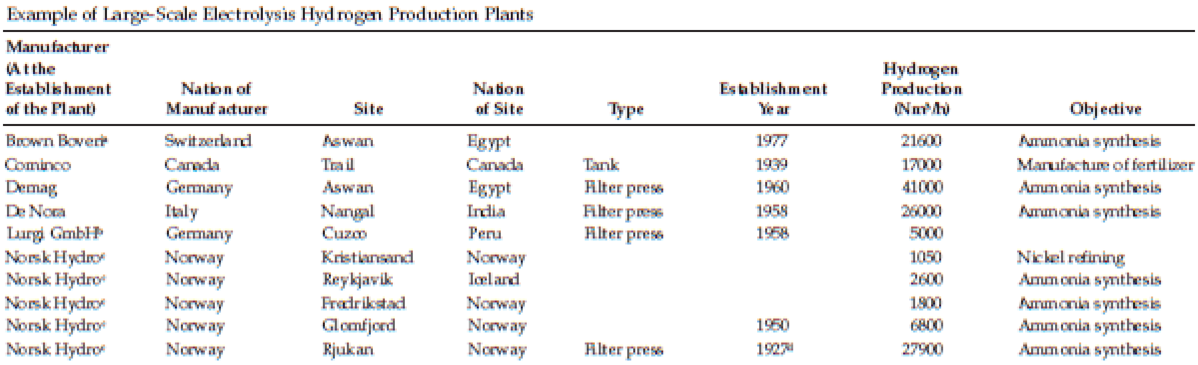
For instance, at the ambient temperature of 25 °C, the reversible and thermoneutral voltages are respectively equal to 1.23 and 1.47 V [92]. For voltages between these values the electrolysis process is isothermal only if it absorbs heat from the outside, while more than 1.47 V, at 25 ° C, the reaction can be isothermal only if heat is removed from the system.

For higher voltages to the potential thermoneutral (Zone 1), reducing the heat removal, or even providing additional heat, it can operate at a higher temperature, reducing the cell voltage, thus achieving a higher electrical efficiency. Consequently higher current density can be used. The heat can be provided, for example, feeding water in the form of steam.

High temperature electrolyte systems are being studied for several years. In particular, since 1977 it has developed a project called Hot Elly (HTE, German Federal Ministry of Research and Technology). The high temperatures (800-1000 °C) operating allow a considerable decrease of the input energy and an increase of efficiency (HTE a plant achieves an efficiency of 92%, while a low temperature system does not exceed 85%).

2.2.4.7.4 High Pressure vs Low Pressure Electrolysers

Industrialization of large-scale AWE is very old. Figure 2-15 shows examples of industrial mass hydrogen-production plants. Sites were selected where low-cost hydroelectric generation and large amounts of pure water were available.



Example of Large-Scale Electrolysis Hydrogen Production Plants

Manufacturer (At the Establishment of the Plant)	Nation of Manufacturer	Site	Nation of Site	Type	Establishment Year	Hydrogen Production (Nm³/h)	Objective
Brown Boveri[a]	Switzerland	Aswan	Egypt		1977	21600	Ammonia synthesis
Cominco	Canada	Trail	Canada	Tank	1939	17000	Manufacture of fertilizer
Demag	Germany	Aswan	Egypt	Filter press	1960	41000	Ammonia synthesis
De Nora	Italy	Nangal	India	Filter press	1958	26000	Ammonia synthesis
Lurgi GmbH[b]	Germany	Cuzco	Peru	Filter press	1958	5000	
Norsk Hydro[c]	Norway	Kristiansand	Norway			1050	Nickel refining
Norsk Hydro[c]	Norway	Reykjavik	Iceland			2600	Ammonia synthesis
Norsk Hydro[c]	Norway	Fredrikstad	Norway			1800	Ammonia synthesis
Norsk Hydro[c]	Norway	Glomfjord	Norway		1950	6800	Ammonia synthesis
Norsk Hydro[c]	Norway	Rjukan	Norway	Filter press	1927[d]	27900	Ammonia synthesis

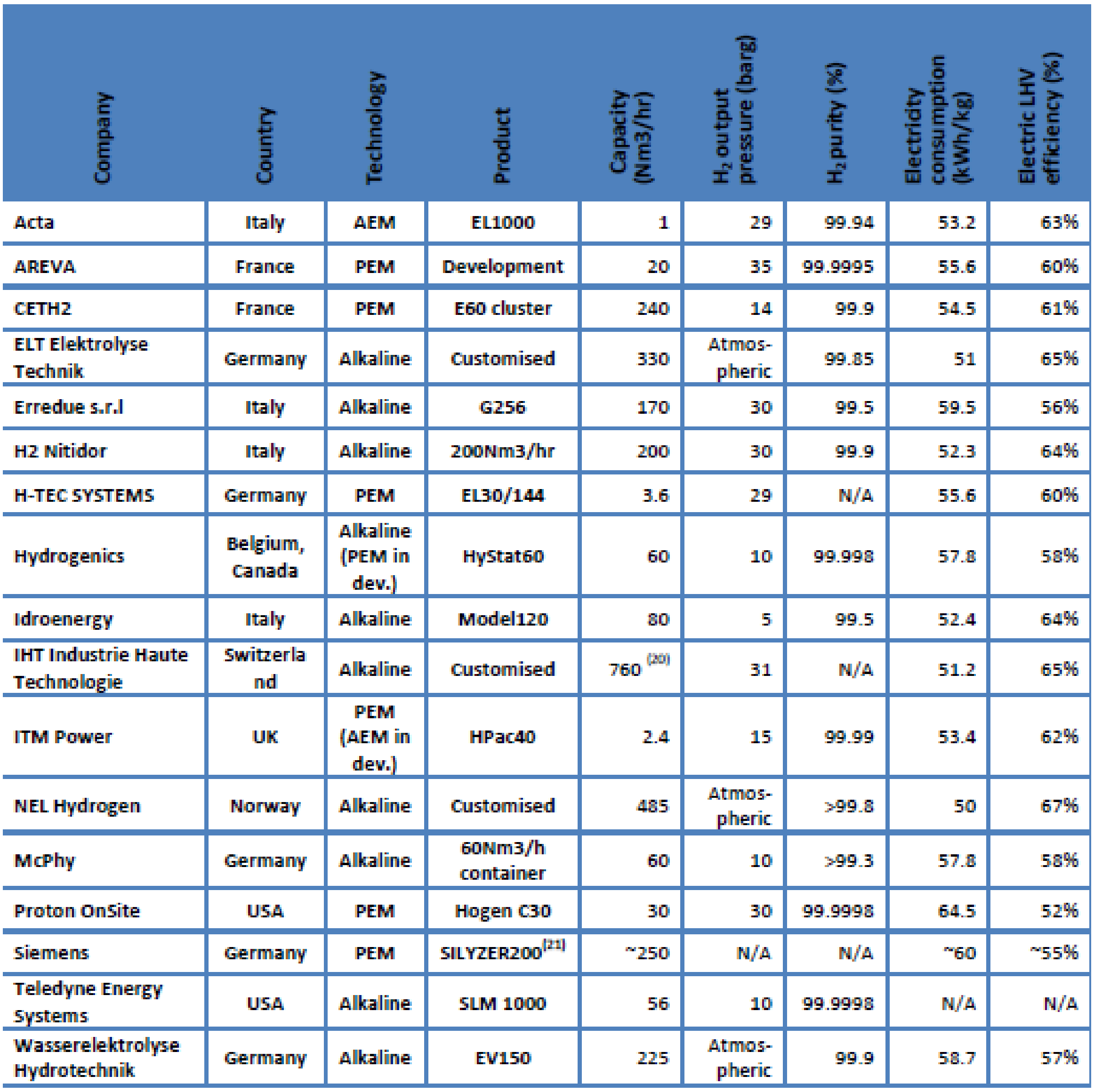
Figure 2-15: Largest Electrolysis Hydrogen production plants worldwide. Adapted from [68]

However, high electricity costs are still detected as the main cause that prevent a large-scale WE hydrogen production in the world [68]. Currently almost all the commercialized EZs operate at ambient pressure, and they require a post-production compression. Lurgi system is the only commercial large-scale pressurized cell [68].

Although a pressurized EZ would let avoid the compression costs, according to [68] the combination of an atmospheric pressure electrolysis cell and a compressor for storage of hydrogen is preferable to pressurized electrolyzer for safety and economy .
Technology of conventional AWE has matured and property has already reached the limit. No significant improvement is expected for this technology in the near future.

2.2.4.7.5 Alkaline Electrolyzers manufacturers

The interest of this thesis work is focused on the Alkaline Electrolyzers (AEZs): a review of the main electrolyser manufacturers and performance data, adapted from [71], [94] is presented in Figure 2-16:



Company	Country	Technology	Product	Capacity (Nm3/hr)	H_2 output pressure (barg)	H_2 purity (%)	Electridty consumption (kWh/kg)	Electric LHV efficiency (%)
Acta	Italy	AEM	EL1000	1	29	99.94	53.2	63%
AREVA	France	PEM	Development	20	35	99.9995	55.6	60%
CETH2	France	PEM	E60 cluster	240	14	99.9	54.5	61%
ELT Elektrolyse Technik	Germany	Alkaline	Customised	330	Atmos-pheric	99.85	51	65%
Erredue s.r.l	Italy	Alkaline	G256	170	30	99.5	59.5	56%
H2 Nitidor	Italy	Alkaline	200Nm3/hr	200	30	99.9	52.3	64%
H-TEC SYSTEMS	Germany	PEM	EL30/144	3.6	29	N/A	55.6	60%
Hydrogenics	Belgium, Canada	Alkaline (PEM in dev.)	HyStat60	60	10	99.998	57.8	58%
Idroenergy	Italy	Alkaline	Model120	80	5	99.5	52.4	64%
IHT Industrie Haute Technologie	Switzerland	Alkaline	Customised	760 (20)	31	N/A	51.2	65%
ITM Power	UK	PEM (AEM in dev.)	HPac40	2.4	15	99.99	53.4	62%
NEL Hydrogen	Norway	Alkaline	Customised	485	Atmos-pheric	>99.8	50	67%
McPhy	Germany	Alkaline	60Nm3/h container	60	10	>99.3	57.8	58%
Proton OnSite	USA	PEM	Hogen C30	30	30	99.9998	64.5	52%
Siemens	Germany	PEM	SILYZER200(21)	~250	N/A	N/A	~60	~55%
Teledyne Energy Systems	USA	Alkaline	SLM 1000	56	10	99.9998	N/A	N/A
Wasserelektrolyse Hydrotechnik	Germany	Alkaline	EV150	225	Atmos-pheric	99.9	58.7	57%

Figure 2-16: AEZs manufacturers and typical modules performance data. adapted from [60]

2.2.5 Solid Oxid Electrolysis Cell (SOEC)

2.2.5.1 High Temperature Steam Electrolysis

Although AWE technology is well developed, the overall hydrogen production efficiency

It has already been shown how increasing the operating temperature, the V_{rev} (but not the V_{TN}) and so the required electric energy decreases. At the limit temperature of 2,500 °C [80] the electrical input is unnecessary because water breaks down to hydrogen and oxygen through thermolysis.

For all the temperatures between 0 and 2,500 °C, the energy input will be a combination of electricity and heat, as explained in the following graphic, that summarizes the Thermodynamics of Steam Electrolysis.

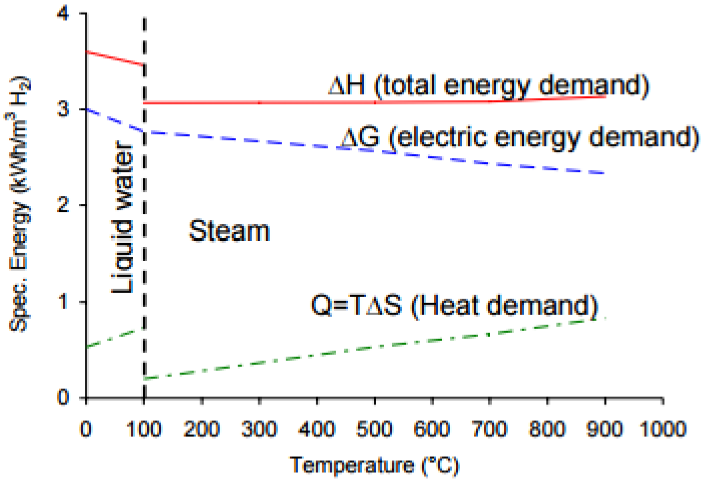


Figure 2-17: Thermodynamics of High Temperature Electrolysis [30]

It is clear from the graphic (Figure 2-17) that the electrolysis is increasingly endothermic with temperature, since the ΔH is an increasing function.

Anyway at ever higher temperatures, a larger fraction of the total energy required for electrolysis, Δ*H*, can be supplied in the form of heat, and this sounds really attractive because:

- Heat is cheaper than electricity (or a less valuable energy form);
- If both electricity and heat are provided by a thermo-electrical power plant, the electricity is itself obtained starting from thermal energy, with a great loss (due to thermodynamic efficiency). So providing directly heat to the HTSE plant, a larger hydrogen production would be achieved.

From a mathematical standpoint, the Gibbs Free Energy and the theoretical Voltage, can be calculated starting from the Nerst equation [30] :

- The Gibbs Free Energy, depending on temperature, composition of electrolyte, and pressure of gas can be written as follow:

$$\Delta G_T = \Delta G_T^0 + RT * \ln\left[\frac{\frac{f_{H2}}{p^0} * \left(\frac{f_{O2}}{p^0}\right)^{0.5}}{a_{H_2O}}\right]$$

- Then the theoretical Voltage is obtained:

$$V_{rev} = V_{rev}^0 + \frac{RT}{2F} * \ln\left[\frac{\frac{f_{H2}}{p^0} * \left(\frac{f_{O2}}{p^0}\right)^{0.5}}{a_{H_2O}}\right]$$

Theoretically, the higher the temperature, the higher the energy efficiency. In practice, materials thermo-mechanical resistance limits the operating temperatures of HTSE at 800-850°C.

Anyway, potential disadvantages of high-temperature operation include the limited availability of very high temperature process heat and materials issues such as corrosion and degradation [30].

There are essentially two ways in which a HTSE plant could operate [97]:

- **Autothermal**: The HTSE should be operated <u>at the thermoneutral voltage</u> (1.29V) or slightly above. The energy for the water splitting is completely supplied by the electric power, providing the electric potential (ΔG) and the heat (TΔS), by mean of the ohmic resistance;
- **Allothermal**: The HTSE is operated <u>below the thermoneutral voltage</u>. The heat requirement (TΔS) for the water splitting is partly supplied by an external high temperature heat source.

It is obvious that the second way is the one that allows to take advantage on the thermodynamics of steam electrolysis that we have just described.

Let us try to clarify this key point, that explains the interest in the HTSE, by mean of a numerical example.

As can be seen in Figure 2-17 the electrical and thermal energy input for the HTSE at 850 °C are roughly, respectively 2.5 and 0.9 kWh/Nm^3 (in terms of theoretical limits), while in the case of AWE it is 3.5 kWh/Nm^3, only electric.

This means that the total energy inputs necessary to produce 1 Nm^3 of H_2, in the AWE and HTSE cases (considering for instance the coupling with a VHTGR) are:

	AWE	HTSE
Electric Energy [kWh_el/Nm^3]	3.6	2.5
Thermal Energy [kWh_th/ Nm^3]	0	0.9
VHTGR TD efficiency	46%	
Total (equivalent) Thermal Energy (VHTGR)	7.7	6.3
Overall efficiency (Thermal to LHV)	38%	47%

Table 2-2: AWE and HTSE energy consumption comparison

The results in Table 2-2 shows how the HTSE is more efficient than AWE, and so if the same power is provided to the two plants, the HTSE plant will produce more hydrogen, which means more revenues.

It also should be noticed that if the NPP had a lower TD efficiency (like a PWR, for instance), the HTSE would take even more advantage on the AWE, since a larger thermal energy would be available.

2.2.5.2 *The SOEC*

2.2.5.2.1 Key components

The key components of an SOEC are a dense ionic conducting electrolyte and two porous electrodes.
The fundamental mechanisms involved in SOEC operation are shown in Figure 2-18.

Electrolysis cell is composed of electrolyte, cathode (hydrogen electrode)and anode (oxygen electrode), as for the WE.

In HTSE reaction, water is warmed up by outer heat *before* entering electrolysis cell as steam.

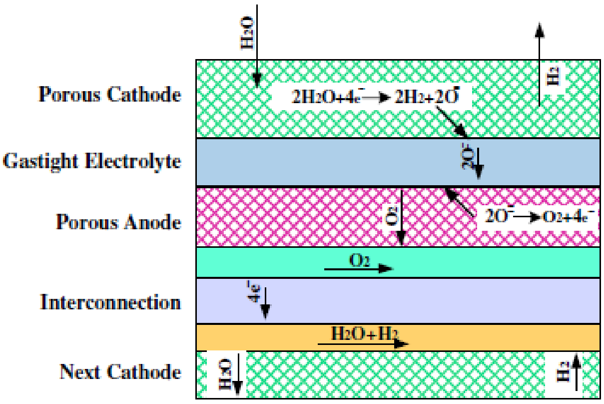


Figure 2-18: Main components of a SOEC

Steam is fed to the porous cathode. When required, electrical potential is applied to the SOEC, water molecules diffuse to the reaction sites and are dissociated, to form hydrogen gas and oxygen ions at the cathode–electrolyte interface. The hydrogen gas produced diffuses to the cathode surface and gets collected. The oxygen ions are transported through the dense electrolyte to the anode. On the anode side, the oxygen ions are oxidized to oxygen gas and the produced oxygen is transported through the pores of the anode to the anode surface [30].

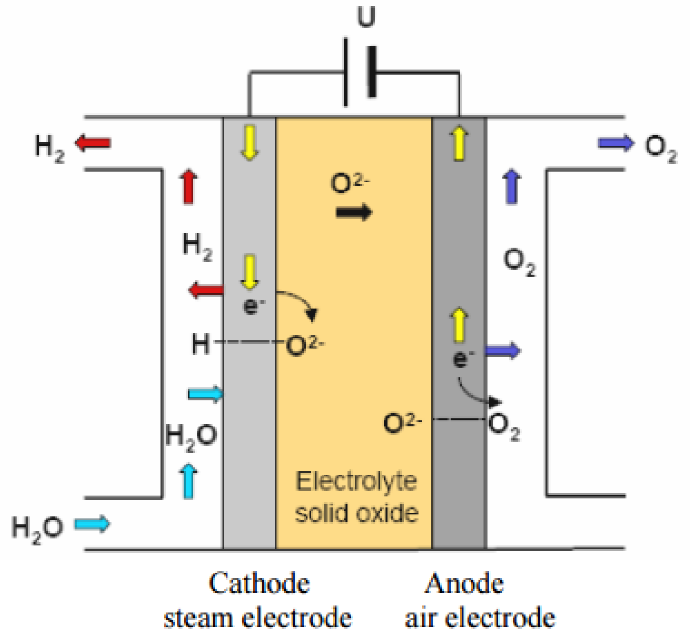


Figure 2-19: Scheme of Process principle of the HTSE

Operating at high temperature, the SOEC components must meet certain requirements for efficient and cost-effective hydrogen production [98]:

- the dense electrolyte should be chemically stable and have good ionic conductivity with low electronic conduction;
- the dense electrolyte must be gastight to eliminate any possibility of recombination of H_2 and O_2, but it should be as thin as possible to minimize the ohmic overpotential;
- both electrodes should be chemically stable in the highly reducing/oxidizing environments and have good electronic conductivity;
- both electrodes should have suitable porosity to support gas transportation;
- the thermal expansion coefficients of both electrodes should be close to that of the electrolyte to prevent high mechanical stresses;
- The cost of the raw materials and the manufacturing cost should be as low as possible.

In the next paragraph, the most used materials for the SOEC are briefly presented.

2.2.5.2.2 Materials

Electrolyte materials

The electrolyte is the essential component of an SOEC. The most common electrolyte material used in SOEC is yttria-stabilized zirconia (YSZ), which exhibits high oxygen ion conductivity and good mechanical strength.
Dopant is added on the zirconia lattice site to stabilize the cubic and tetragonal structures and to increase the concentration of oxygen vacancies so as to increase the oxygen ion conductivity.
It can be seen that the electrolyte has high conductivity when it is doped with Y_2O_3, Yb_2O_3, and $Sc_2\ O_3$ [98].
ScSZ also has a very good ion conductivity, but it is not widely used as an electrolyte for high temperature operation mainly because of its high cost [99].
For comparison, YSZ is much more economical and offers the best combination of ionic conductivity and stability, and, thus, is the material of choice for SOEC electrolyte.
The ionic conductivity of the electrolyte is influenced by the concentration of the dopants. The maximum oxygen ion conductivity of YSZ can be obtained when the molar fraction of Y_2O_3 is around 8% [100].
Other materials have been considered for the electrolyte: the doped $LaGaO_3$ has proved to have good ion conductivity, and could be a promising electrolyte for intermediate-temperature steam electrolysis, but its main problem is its reactivity with Ni electrode
to form lanthanum nicklates [98]. Also the Ceria-based oxides are under experimentation, as electrolyte materials.

Cathode materials

The cathode of an SOEC supports diffusion of steam and hydrogen gas and provides active sites for steam reduction.
Noble metals , such as Pt, and non-precious metals, such as Ni and Co, can be used as SOEC cathode.
Noble metals are not preferred due to its [98]:

- high cost;
- formation of volatile oxides;
- aging of porous structures at a high temperature.

Ni is largely used in SOEC, thanks to its high electrochemical reactivity [98].
Although Ni can induce hydrogen reduction, it only conducts electrons. As a result, the electrochemical reactions only take place at the triple-phase boundary of the cathode–electrolyte interface.
In order to extend the electrochemical reaction zone, the Ni particles can be mixed with ionic conducting particles, usually the same material as the electrolyte, such as YSZ.
This type of electrode is called cermet electrode and is presently widely used.

Anode materials

Only two classes of materials are feasible as SOEC anode materials under highly oxidizing environments [98]: (1) noble metals such as Pt and Au; and (2) electronically conducting

mixed oxides.
Noble metals are excluded due to cost considerations. Thus, only some electronically conducting oxides are suitable materials for using as SOEC anode.
So far, the most commonly used anode materials are mixed oxides with perovskite structure, such as the lanthanum strontium manganate.

2.2.5.2.3 Stack configuration

The single cell of SOEC and can be in either tubular or planar configuration, as shown in Figure 2-20. Conventional SOEC cells are made in cylindrical shape [101] [102][103].

In the tubular SOEC, steam is fed through the inside of the tube and reduced to hydrogen gas and oxygen ions. The oxygen gas is extracted from the outer layer of the tubular SOEC. Compared with planar SOEC, the tubular SOEC exhibits higher mechanical strength and facilitate sealing.

Despite larger sealing length between anode and cathode compartment, the planar cells have received more and more attention in recent years due to their better manufacturability.
Hino et al. [104] found that the planar SOEC performed significantly better than its tubular counterpart. It is because the distribution of gas species on the planar SOEC is more uniform. This suggests that planar configuration deserves to be further investigated.
In order to increase the hydrogen production rate, the active area of the EZ should be increased. As it is difficult to achieve this task by simply increasing the single SOEC dimension, it is important to connect a large number of single cells to build a desired stack.
A large electrolysis stack with tubular SOECs in a serial connection has been tested and demonstrated to be feasible [103].

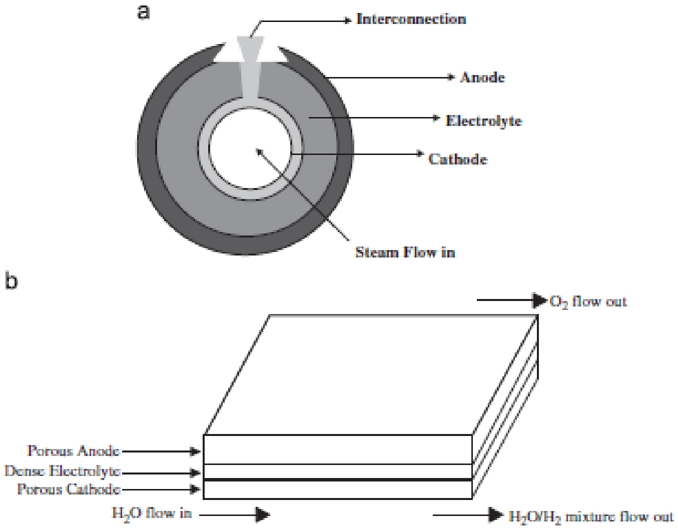


Figure 2-20: SOEC configurations—(a) tubular SOEC (end view) and (b) planar SOEC.

Regarding the operation modes, a clarification is necessary: while the standard-state open-cell potential calculation refer to the case in which pure reactants and products are separated and at one standard atmosphere pressure, in most of practical HTSE systems this do not happen.

The incoming steam is usually mixed with some hydrogen and possibly some inert gas. Some inlet hydrogen is normally required in order to maintain reducing conditions on the steam-side electrode, typically a nickel cermet.
Also, it is not desirable to run the electrolyzer to 100% steam utilization, because localized steam starvation will occur, severely degrading performance. Therefore, the outlet stream will include both steam and hydrogen.
Residual steam can be removed from the product by condensation [68].

2.2.5.2.4 R&D challenges

Even though [105] says the first commercial high temperature electrolysis plants is expected to be available around 2020-2025, HTSE is relatively new technology, still under R&D.

The state-of-the-art of SOFCs have advanced significantly in recent years; SOEC technology has also benefited from the advancement of SOFCs, but relatively little direct funding has been available for SOEC research.
The ultimate cost of hydrogen production by any technology is dependent on both capital and operating costs. In order to achieve competitive capital costs, HTSE cells and stacks must exhibit both high performance and low degradation rates. In particular, very low degradation rates of less than 1% per 1000 h will be required for viable large-scale hydrogen production [30].

According to [106] the first priority should be intensive efforts to acquire reliable data in the fields of thermodynamics, kinetics, material behavior, and electrochemical performance to support simulation and technological optimization.
Furthermore, there are not enough SOEC models to perform optimizations by numerical simulations, which let the experimental research proceed faster.
Several technological aspects that are still far to be solved, prevent for now the debut on commercial scale of the SOEC.

[107] from Idaho National Laboratory (INL) asserts that the stack performance degradation over time has been identified as the major barrier to technology development.
SOEC stack testing performed at INL to date has exhibited high degradation rates.
Anyway, at present, a complete understanding and general agreement on the causes of degradation in SOECs and the electrochemical and physical mechanisms behind them does not exist.

2.2.5.3 SOEC coupled with a NPP

Since the HTSE is an high temperature application, it has largely been considered to be coupled with a VHTGR [108], [109].

The principle scheme of a plant conceived like this is presented in the following Figure 2-21.

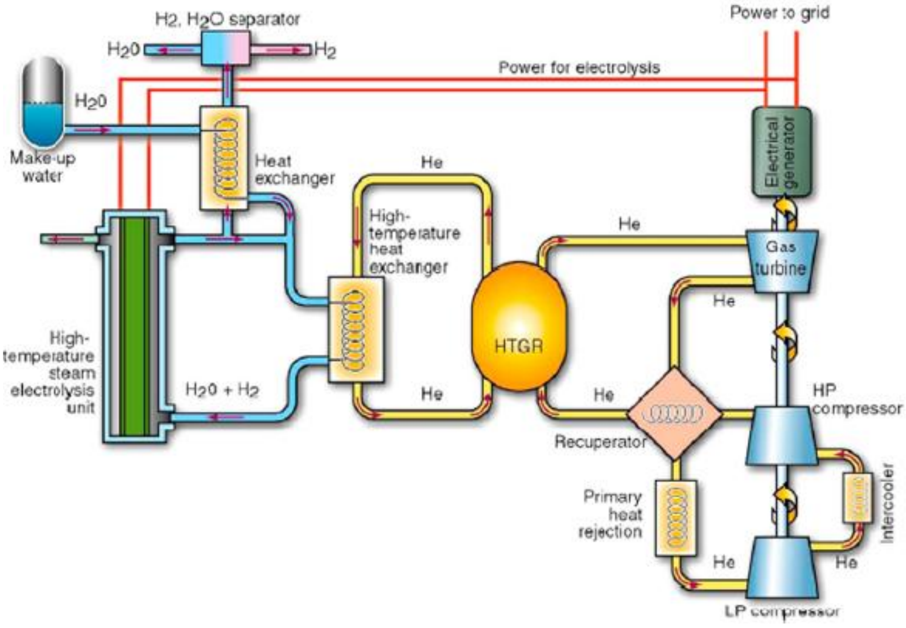


Figure 2-21: Conceptual scheme of a NPP - HTSE coupling

Essentially the process consists of the VHTGR to produce high temperature thermal energy, the power cycle to generate electricity, the heat exchanger to supply thermal energy to the superheated steam generator, the high temperature electrolyzer to produce hydrogen from steam, the heat-recuperating condenser, the hydrogen–water separator, and the dehumidifier to remove the residual water from the hydrogen.

The high temperature heat exchanger supplies superheated steam to the electrolyzing cell at a temperature of around 850 °C, and a pressure between 35 and 50 bar, depending on the considered design [96].
The incoming water stream is vaporized and preheated in the electrolysis recuperator, which recovers heat from the postelectrolyzer process.
Downstream of the recuperator, the steam is mixed with recycled hydrogen product gas. A fraction of the product gas is recycled in this way in order to assure that reducing conditions are maintained on the steam/hydrogen electrode (cathode). Argon gas can be used as an inert carrier gas. The argon and hydrogen mixture is mixed with steam to maintain the proper humidity and partial pressures of the gas mixture [108].
Downstream of the mixer, the process gas mixture enters the IHX, where final heating to the electrolysis operating temperature occurs, using high-temperature process heat from the nuclear reactor. The process stream then enters the electrolyzer, where the steam is electrolytically reduced [108].
Downstream of the electrolyzer, the hydrogen-rich product stream flows through the electrolysis recuperator where it is cooled and the inlet process stream is preheated.
The hydrogen stream separated from the condensed water is introduced into a dehumidifier and finally stored in a storage vessel, except for a fraction of the product gas is recycled into the inlet process stream [108].

In the design represented in Figure 2-21 there are two separated Helium flows that leave the core:

- the flow on the *right* goes directly to the Gas Turbine, and leads to electricity production;
- the flow on the *left* is delivered to a High Temperature Heat Exchnger, that heats the water (from the liquid phase) and turns it into high temperature steam.

A design like this, is conceived to perform a cogenerative coupling (the SOEC operate 24 hours per day). While, if the aim is to perform Load Following, there should be a partializing valve, so that a part the hot Helium is delivered to the Heat Exchanger just during the night.

The reactor thermal power assumed for the high-temperature helium-cooled reactor is currently 600 MWt [68].
The primary helium coolant exits the reactor at 900°C. This helium flow is split, with more than 90% of the flow directed toward the power cycle and the remainder directed to the intermediate heat exchanger (IHX) to provide process heat to the HTSE loop (≈ 60 MWt).

2.2.6 Sulfur-Iodine Thermochemical cycle

2.2.6.1 Sulfur-Iodine cycle

The SI process was originated and still developed by US General Atomics. It is composed by three chemical reactions, as follows [30]:

I. Production of two acids, at 100 °C

$$SO_{2(g)} + I_{2(l)} + 2H_2O_{(l)} \rightarrow 2HI_{(aq)} + 2H_2SO_{4(aq)};$$
$$\Delta H_I = -98\ kJ$$

II. Decomposition of sulfuric acid, at 900 °C:

$$H_2SO_{4(aq)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \frac{1}{2}O_{2(g)};$$
$$\Delta H_{II} = 329\ kJ$$

III. Decomposition of hydriodic acid, at 450 °C:

$$2HI_{(aq)} \rightarrow H_{2(g)} + I_{2(g)};$$
$$\Delta H_{III} = 119\ kJ$$

So, the net reaction results:

IV. $H_2O = H_2 + \frac{1}{2}O_2;\ \Delta H_{IV} = 286\ kJ$

In the calculation of reaction enthalpy, ΔH, $H_2SO_{4(aq)}$ means the , H_2SO_4 in the aqueous solution which has molar ratio of H2SO4:H2O, H_2O = 1:4.
$HI_{(aq)}$ is the HI in the solution where the molar ratio is HI:I_2:H_2O = 1:4:5.

The process scheme of the SI cycle is shown in Figure 2-22.
Reaction *I* (known as the Bunsen reaction) is exothermic: the feedwater (which in Figure 2-22 enters from the bottom) is made react with reagents iodine (I_2) and sulfur dioxide (SO_2) with the spontaneous production of hydriodic acid (HI) and sulfuric acid (H_2SO_4) at a relatively low temperature (approximately 100 °C).
Then the two acids follow different loops [30]:

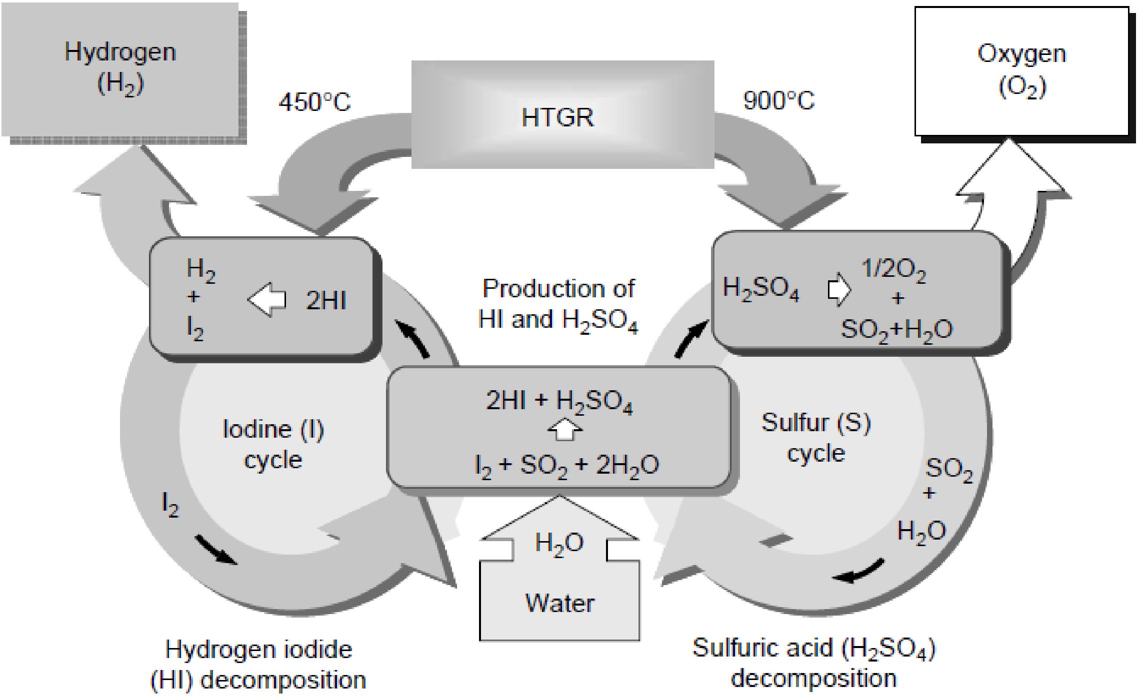


Figure 2-22: Principle scheme of the SI cycle [34]

- The sulfuric acid (Sulfur cycle) is heated until approximately 900 °C, where the reaction *II* takes place and it thermally decomposes releasing oxygen;
- The hydriodic acid (Iodine sycle) is heated until 450 °C, where it decomposes according to reaction *III* and releases hydrogen.

All other products of these two reactions are recycled back to reaction *I* to resume production of the acids.
A closed process is completed with the net effect of reaction *IV*.

It must be underlined that the process is still under R&D, and different sources report differ temperatures and ΔH of chemical reactions [70], [78]. Anyway, for this study, the values reported above are taken for the energy balances (see 3.5.1).

The SI process has a relatively small number of reactions and can be a pure thermochemical process with all fluid materials. These features simplify scale-up and operation in the practical plant [30].

By this process the hydrogen can be produced with an overall efficiency of 45% based on the higher heating value of hydrogen [110].

2.2.6.2 Sulfur-Iodine Thermochemical Plant: R&D issues

A SI thermochemical (hypothetical) plant simplified flow sheet is shown in Figure 2-23, taken from [111].
The water as a raw material is supplied to the Bunsen chemical reactor. This chemical reactor produces a mixed acid, that are sent to the liquid–liquid separator in which they are settled; and because of the presence of excess iodine, the mix separates into two types of

acid. The acid, which is rich in HI, the HI*x* phase, is fed into the HI decomposition section, while the acid, which is rich in H_2SO_4, the H_2SO_4 phase, is fed into the H_2SO_4 decomposition section [111].

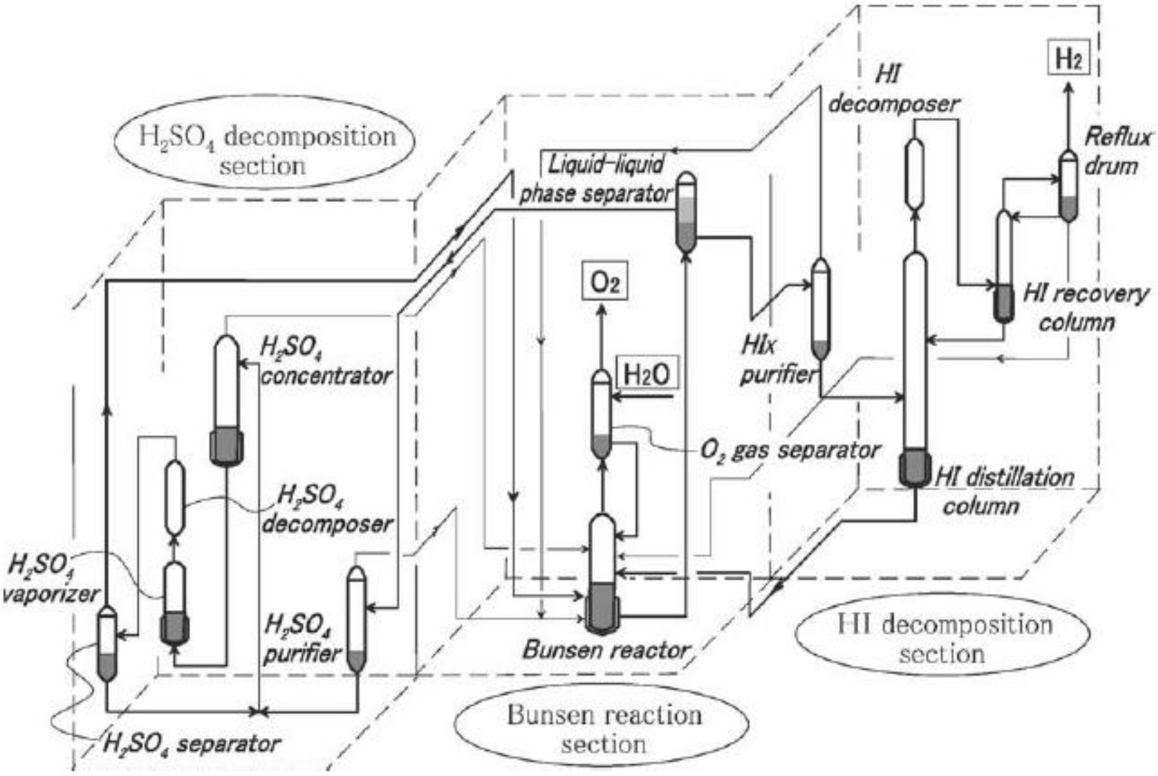


Figure 2-23: Sulfur-Iodine Plant simplified flow sheet

The functions of the HI decomposition section are to produce hydrogen and to recycle the products except for hydrogen. In this chemical reactor, H_2 and I_2 are produced from HI using a platinum catalyst. The products flow into the HI recovery column; the bottom is refluxed to the HI*x* distillation column, while the hydrogen with the H_2O vapor leaves from the top. The H_2O condenses and is recycled into the Bunsen chemical reactor, while hydrogen leaves the facility. [111]. The H_2SO_4 purifier removes HI as an impurity from the H2SO4 phase, where the reverse reaction of the Bunsen reaction takes place by heating. The purified H_2SO_4 reaches a concentration of 90% in the H_2SO_4 concentrator by heating; The concentrated H_2SO_4 vaporizes in the H_2SO_4 vaporizer that connects with the H_2SO_4 decomposer. In this chemical reactor, O_2 with SO_2 and H_2O are produced from H_2SO_4 in the presence of a catalyst bed of platinum. The H_2SO_4 separator separates them into undecomposed H_2SO_4 and gaseous components of O_2, SO_2 and carrier gas by cooling; the former is reused to be concentrated in the H_2SO_4 concentrator, the latter for recycling in the Bunsen chemical reactor.
Currently, there is no operating Sulfur-Iodine Thermochemical Plant; nevertheless not only the component reactions, but also the entire cycle actually works [112].

Anyway, beforming succeeding in scaling up to a large plant, several issues must be solved. In the last years the research has been carried out in the following fields [34]:

- Study on the chemistry of each reaction section;

- Demonstration of the closed-cycle hydrogen production;
- Heat/mass balance analysis of the process flow sheet;
- Screening of corrosion-resistant materials.

As for the chemical reactions, the main problem is the separation of hydriodic acid and sulfuric acid produced by the Bunsen
Reaction. To solve this issue, researchers of GA found that the mixed acid solution

produced by the Bunsen reaction separates spontaneously into two liquid phases in the presence of excess amount of iodine [113].

As for the demonstration of the closes cycle, researchers at JAEA successfully demonstrated a stable and continuous hydrogen evolution carried out with the rate of 1 liter hydrogen [112].

The heat/mass balance influences the efficiency of the process: Norman [113] estimates the overall thermal efficiency as 47% for a process featuring LL (liquid-liquid) separation in the Bunsen reaction section; however several different values ranging from 33 to 57% are reported in literature [68].

Because sulfuric acid and halogen are very corrosive, selection of the structural materials is an important and still open issue. Screening tests have been carried out using test pieces of commercially available materials at GA [114] and JAEA [115].

Despite the difficulties, particularly in United States, France, Korea, as well as Japan, R&D on thermochemical water splitting process, especially SI cycle, is ongoing [116], [117].

2.2.6.3 SI Plant coupled with NPP

The coupling between a SI plant and a VHTGR is studied in [118].
The GTHTR300C generates up to 300 MWe electricity at 45-50% thermal efficiency by a direct cycle gas turbine power conversion system and up to 1.4 million Nm^3 hydrogen / day at about 45% efficiency by the SI process, or cogenerates both electricity and hydrogen in these ranges.
The reactor is rated 600 MWt thermal power and 850~950 °C reactor outlet temperatures.
By an intermediate heat transport loop, a share of the high temperature reactor heat is delivered in piping as high temperature process heat to the adjacent hydrogen plant.
The hydrogen plant should be sited close to the reactor building to shorten the high temperature heat transport piping whose specific cost is high [118].
Also safety issues have to be taken into account: the best means to meet the design requirement of a separation distance between the plants within 100 m the GTHTR300C are the following:

- To erect a protection wall near hydrogen plant to prevent hydrogen dispersion by diffusion;
- To clear any packed obstacles in the separating space between hydrogen and reactor plants.

2.3 Electrolytic hydrogen production costs

As Felgenhauer et Hamacher show in their study [69] on Alkaline and PEM WE costs, over a computed cost of 5.4 $/kg_$H_2$ produced, the Electricity cost accounts for 4$, so for the 74%, approximately (seeFigure 2-24) . Clearly this values is different for each investment, but it is indubitable that the supply of electric energy largely represents the main cost item for the hydrogen production by Water Electrolysis.

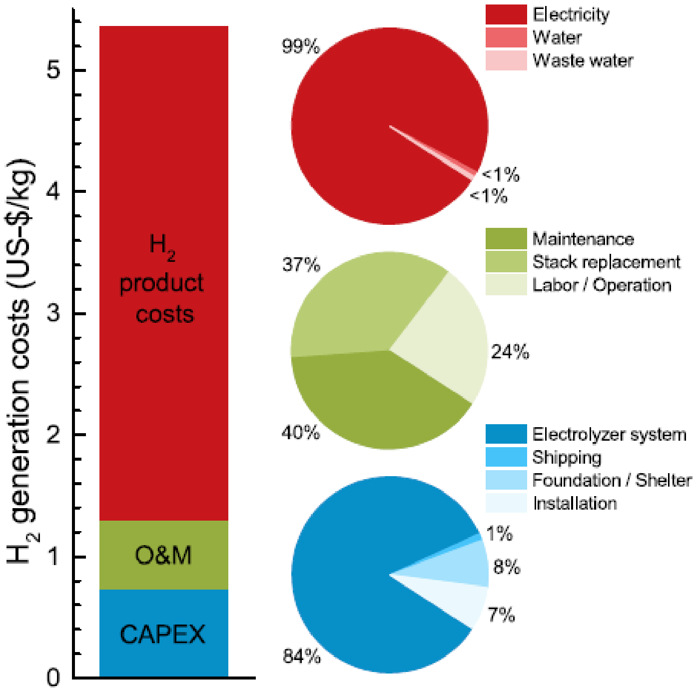


Figure 2-24: H_2 generation costs for an AEZ with 100% capacity utilization [69]

Since the cost of electricity is local parameter (it depends on the Electricity Market of the country where the plant operates), this literature review of the AWE costs does not consider it, but focuses only on the Capital Cost of the Alkaline Electrolyzers (AEZs), on the Operation & Maintenance (fixed) Costs, which include all the Non-Electrical costs.

Furthermore, the Stack Replacement, i.e. the substitution of the part of the EZ where the electrochemical reactions actually take place, is necessary after a period of operation varying between 6 and 11 years, depending on the system [69]. The data found in literature regarding this cost item are treated separately.

2.3.1 Capital Cost

According to [71], which is the report of the reference for the water electrolysis cost, even for several companies operating in the sector, the available alkaline electrolyser systems (in 2014) cost ranged between 1,000 to 1,200 €/kW, plus installation, while it is expected to decrease to 760—1,100 €/kW by the 2015.
A significant reduction in costs is expected in the next 5 years, which could also be guided and facilitated by growing penetration of hydrogen as a fuel in the automotive market.

The forecast capital cost in 2020 is 600 €/kW, with optimistic previsions of 370 €/kW (best case) [71].

To put these significant expected cost reductions into context, it is important to note that today, electrolysers are built in small volumes for niche markets.

Electrolyser companies have limited supplier choices and often Balance of Plant components designed for other industrial applications have to be bought, which may be both more expensive than they could be and inappropriate for the specific needs of an electrolyser system [71].

For the AWE, which is considered a mature technology, it is expected that much of the cost reduction potential comes from an improved supply chain, and through increased production volumes for which more cost-efficient production techniques can be used [71].

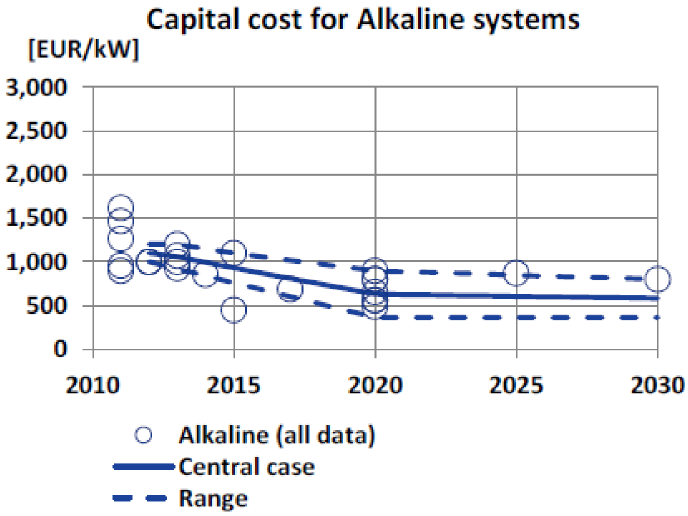


Figure 2-25: Capital Cost trend of Alkaline Electrolyzers

As for the present values, it is worth to underline a concept regarding the size of Electrolyzers (EZs): as large-size EZs are intended those electrolyser units with a power input (roughly) ranging between 0.35 and 3.5 MW electric [69]. This is due to the consolidated awareness that centralized large electrolysis plant are not economically competitive, as discussed in section 2.2.3.

So, if there is a need for a WEP of a size exceeding some MW, several modules are required.

Since the typical modularity shown by Large alkaline electrolyzer installations, they do not show a significant economy of scale.

Anyway, substantial capital cost reductions are possible if electrolyzer stacks utilize equipment common to each modular installation: [119] shows that scaling the compressors, the gas holding tanks, the transformers and the balance of plant equipment can reduce the capital costs by as much as 60% for the best-case scenario and 25% for the worst-case scenario, as can be seen in Figure 2-26.

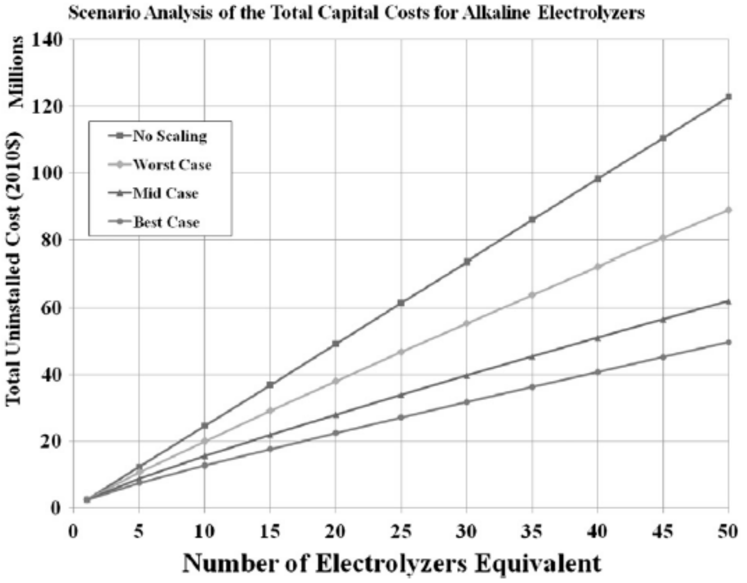


Figure 2-26: The effect of different scaling exponents on the uninstalled costs of Alkaline Electrolysers

MW-size EZ units are sold by several EZs manufacturers (namely: CETH2/Areva H2Gen, Hydrotechnik, Hydrogenics, ITM Power, McPhy Energy, NEL, Next Hydrogen, PERIC, Siemens). The prices of the single units are generally not available on internet, and have to be asked directly to the manufacturers: mostly they fall in the range provided by [71].

Trying to forecast the cost of a large-scale Water Electrolysis Plant (WEP) requiring a large number of units, is the real challenge, both for manufacturers and researchers.
This is due to the limited experience in the large-scale EZs field, the limited number of units produced and sold in the current market (for instance, it should be taken into account that a demand of hundreads of MW-size EZs would cover many times the annual production of a typical manufacturer company ([63] 18.) and the necessity to design and estimate the cost of the auxiliary equipment for a large plant [120].

As for this thesis, the reference capital cost has been obtained from a direct contact with the manufacturer of the chosen EZ unit ([63] 15., 16.), whose technical specifications have been used in the model (see **Errore. L'origine riferimento non è stata trovata.**).

2.3.2 Operation & Maintenance (Non Electrical) Costs

Often these costs are provided as a percentage of initial capital expenditure (% of capex per year). According to [71] OPEX ranges between 2-5% of capex per year.
Anyway, these values this number are very sensitive to location (labour cost) and size. In Table 2-3 is presented the decrease of OPEX with the rise of the size.

Plant Size	OPEX
[MW]	[% of initial capex per year]
1	5.0 %
5	2.2 %
10	2.2 %
20	1.85 %

50	1.64 %
100	1.61 %
250	1.54 %
1,000	1.52 %

Table 2-3 : Water Electrolysis Plant OPEX dependence on size

Also manufacturers confirm O&M costs ranging between 1.0 and 1.5 % for a large WEP ([63] 18., 21.).

2.3.3 Stack Replacement Costs

While manufacturers do not share their in-house data on cost breakdowns, [71] asserts that stack costs typically contribute about half of the overall costs in both alkaline electrolysis, as shown in Figure 2-27:

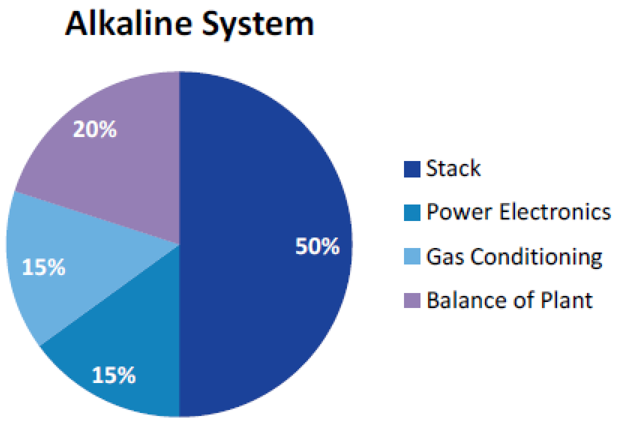


Figure 2-27 : Indicative Electrolyser unit cost breakdown

Since the plant life is estimated to 40 years ([63] 16.), but the EZs last only 10 years ([63] 16., 18.), the stack has to be changed to renew the plant. From this standpoint, the EZ cost breakdown (even though approximated) is the most useful data to forecast the impact of the Stack Replacement cost. Moreover it also meets the estimated of the suppliers ([63] 16., 18.).

2.4 Reserve Services and Energy Storage

As already explained in the Introduction, the Electric Grid service company of any country has to face a variable energy demand. The focus of this thesis is the UK market, where the National Grid procures Balancing Services in order to balance demand and supply and to ensure the security and quality of electricity supply across the GB Transmission System.

National Grid need to access to sources of extra power in the form of either generation or demand reduction, to be able to deal with unforeseen demand increase and/or generation unavailability. These additional power sources available to National Grid are referred to as Reserve. Different sources require different timescales in order to be ready to deliver the services [121].

2.4.1 Reserve Services provided by National Grid

As [122] summarizes, the main reserve services that UK National Grid provides are:

1. *Fast Reserve*, that is used in addition to other energy balancing services to control frequency variations that might arise from sudden, and often unpredictable, changes in generation or demand. Regarding Fast Reserves, active power delivery must start within 2 minutes of the dispatch instruction and the reserve energy should be sustainable for a minimum of 15 minutes. It must be able to deliver minimum of 50MW.
2. *BM Start Up*, that consist of:
   - *BM Start Up***,** that has the ability to prepare the generator towards a state of readiness in order to synchronize the unit within Balancing Mechanism timescales (89 minutes from instruction).
   - *Hot Standby***,** that maintains the unit in a state of readiness, for an agreed period of time, in order to synchronize to the system within Balancing Mechanism timescales.
3. *Frequency Response*, that controls second-by-second the system frequency and the balance between system demand and total generation. If demand is greater than generation, the frequency falls, while if generation is greater than demand, the frequency rises. National Grid has the obligation to control frequency within the limits specified in the Electricity Supply Regulations, i.e. ±1% of nominal system frequency (50.00Hz).
4. *STOR***,** whose minimum capability requirements are:
   - offer a minimum of 3MW generation;
   - have a maximum Response Time for delivery of 240 minutes, although typical contracts are for 20 minutes or less, as shown in Figure 2-28;
   - be able to deliver the contracted MW for a continuous period of minimum 2 hours;
   - have a recovery period after provision of Reserve of not more than 1200 minutes;
   - be able to deliver at least 3 times per week.

Primary Reserves are used to stabilize the system frequency at a stationary value within a few seconds, as UCTE policy sets the minimum total frequency deviation to 0.8 Hz, and must be delivered until the power deviation is fully offset by the Secondary and Tertiary Reserves; *Secondary Reserves* have to start within the 30 seconds following the disturbance period, and respond to the imbalances within 15 minutes; *Tertiary Reserves* are used after Primary and Secondary Reserves, which explains why they are also called *15-minutes reserves*, although there is no recommendation on the required time when these reserves must be fully activated.

In UK, the National Grid has to guarantee operating reserves from 4 hours ahead to real time, in order to take into account load uncertainties and market imbalances. Reserve services requirements are met accepting bids and offers through the Balancing Mechanism and can be listed according to their time of response. STOR services have a maximum response time for delivery of 240 minutes, although typical contracts are for 20 minutes or less, as shown in Figure 2-28.

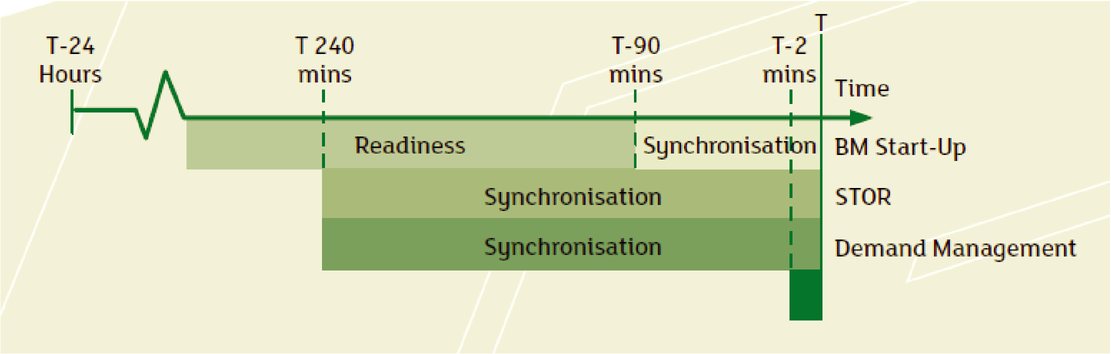


Figure 2-28: National Grid Reserve services summary

The need of STOR depends on the time of the year, the time of the week and the time of the day. UK National Grid splits the year into six seasons and divides the days of the week into *working days* and *not-working days*, and for every seasons and days the National Grid specifies the hours in which the operating reserves are required. The periods in which STOR are required are defined *availability windows.*

There are two forms of payment that National Grid will make as part of the STOR service [123]:

1) *Availability Payments* (£/MWh), where a reserve provider is paid for the units that he makes available for the STOR;

2) *Utilisation Payments* (£/MWh), where the reserve provider is paid for energy actually delivered.

The payment data for STOR and FR are presented in Table 2-4 and Table 2-5, respectively:

STATUS: Short Term Operating Reserve	Availability (contracted)	Utilisation	Not Contracted
Hours per year	3,864	78	4,818
Unitary payment [£/MWh]	2.45	155	0

Table 2-4: Short Term Operating Reserves - Payment summary (National Grid tendering data [123])

STATUS: Fast Reserve	Availability (contracted)	Utilisation	Not Contracted
Hours per year	4,223	365	4,912
Unitary payment [£/h] For a 99 MW Reserve plant	594	140	0

Table 2-5: Fast Reserve - Payment summary summary (National Grid tendering data [124])

2.4.2 Energy Storage Systems (ESS)

Akinyele and Rayudu [125] give a complete overview of ESS. This process enables energy to be stored at times of either low demand, low generation cost or from intermittent energy sources and use it at times of high demand, high market price and or when power is needed as backup.

A storage system is made up of four main components: the charging unit, the storage medium, the discharging unit, and the control unit. As shown in Figure 2-29, storage technologies can be classified by the form of storage into four different main clusters: mechanical (such as Pumped Hydroelectric Storage (PHS), Compressed Air Energy Storage (CAES), chemical (fuel cells, batteries..), electrical (capacitor, super capacitors), and thermal [126][127].

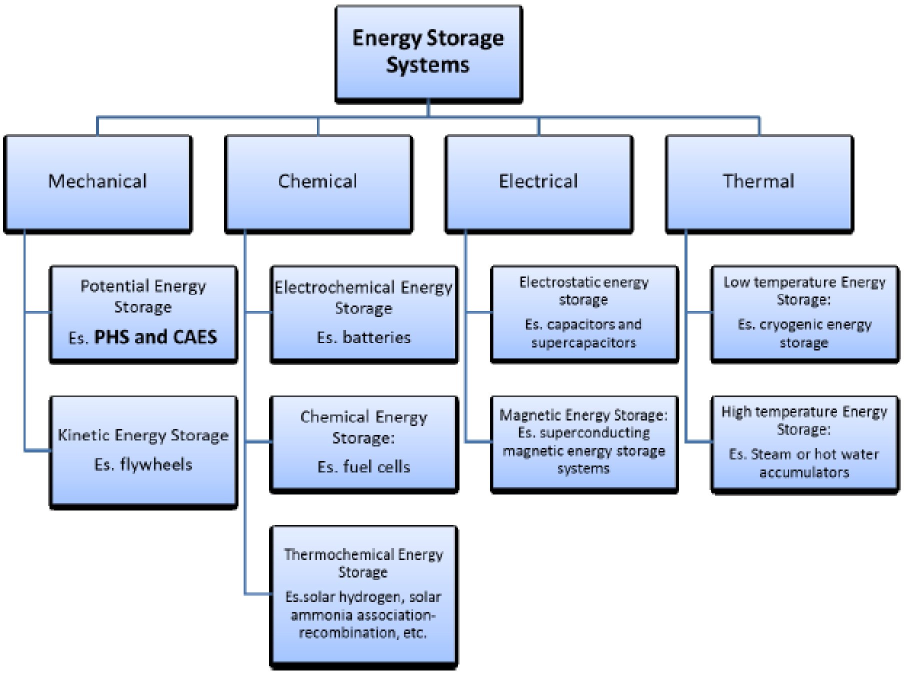


Figure 2-29: Energy Storage Classification

It is hard to have a complete overview of the number of ESS installed in the world and their capacity [128]. The two most relevant and continuously updated database are [129], from the Department of Energy, and from the Energy Association of Storage of Energy [130]. Even if some differences between these sources exist, the key messages are:

1. 140 GW of large-scale ESS is currently installed worldwide [128];
2. 99% of ESS capacity consist of PHS technologies [128];
3. 1% of ESS include a mix of mix of battery, compressed air energy storage, flywheels, and hydrogen storage [129].

We do not investigate further on ESS, since this is not the purpose of this thesis work. We just want to underline that currently the balancing services are performed by mean of the ESS, which ‘confine’ energy in a certain form and in a certain ‘container’, and use it when it is necessary.

On the contrary, this study proposes to use hydrogen production by AWE *like an energy storage system*, selling EE on the Reserve market; but, in this case, no energy is actually stored anywhere. This concept will be clarified in the section 3.3.

3 Sizing – Technical perspective

In this chapter, first technical results of this dissertation are discussed.
Firstly, a table summarizing the essential characteristics of the three hydrogen production technologies that are the object of this thesis work is presented.
Then, for each technology some technical considerations are made, and an analysis regarding the sizing of the plants, the annual energy consumption and so the annual hydrogen production is conducted.
In particular, the aim of this step is to calculate and list all the power requirements and technical values which represent the technical inputs in the economic balance sheets.

3.1 Scenario definition

After having considered several possible by-products (and the related processes) for the coupling, we focused our efforts on the hydrogen production by water splitting (see section **Errore. L'origine riferimento non è stata trovata.**), and more specifically on:

- Alkaline Water Electrolysis (AWE);
- High Temperature Steam Electrolysis (HTSE);
- Thermochemical Water Splitting: signally the Sulfur Iodine cycle (SI cycle).

Regarding the energy input, AWE requires only electricity (about 4-4.5 kWh_el [30] per Nm^3 of H_2, which roughly means 12-13 kWh_th equivalent) and takes place at low temperature. So it presents the disadvantages of an electrical application (see section **Errore. L'origine riferimento non è stata trovata.**), but this allows to propose the usage of a WEP to sell energy on the Electricity Reserves Market, as will be explained in section **Errore. L'origine riferimento non è stata trovata.**.

On the contrary, both the HTSE and and the SI cycle take place at high temperature (approximately 850 °C [30]). Anyway there is a great difference in the power supply between HTSE and SI cycle: indeed HTSE requires a combination of electric and thermal energy (≈2.5 kWh_el + 0.9 kWh_th [30], so ≈8.5 kWh_th equivalent, of whom electricity is the most part: 88%, this makes HTSE an almost-electrical application), while for the SI cycle only thermal energy (5.9 kWh_th [30]) is needed.

As for the coupling three NPPs have been considered: a SMR PWR (e.g. IRIS), a LR PWR (e.g. EPR) and an SMR VHTGR (like GTHTR300).

For the electrical application, since the NPPs have been resized (see section 3.2) in order to make the economic assessment at the same electric power output, there is no difference between the NPPs, and no advantage in using an SMR in place of a LR.

On the other hand, for thermal applications, [12] has proven that SMRs are more suitable from an economic point of view, so we just study the coupling with the SMR PWR and the SMR VHTGR.

Now the technical feasibility of the coupling is discussed.

The AWE is a feasible and commercial available technology, whose electric power input can be provided by any source: the economic profitability of its coupling with nuclear, PV, and wind plants is under investigation [31], [131];

The HTSE is a feasible process performed into a SOEC. SOECs are under R&D, in particular because of excessive degradation issues. Being an high temperature electrochemical reactor, the SOEC has always been conceived to be put beside an high temperature NPP. Anyway [46] suggests that an SMR PWR like NuScale can also be used to produce hydrogen and oxygen via steam electrolysis.

In the case study proposed by [46] heat and electrical power produced by a NuScale power module (NPM) was directly routed to a proportionally scaled HTSE unit operating at 800°C. A tertiary steam loop by-pass was added to the NPM power cycle steam delivery loop to transfer heat to the HTSE plant. Condensate produced in the HTSE loop was recombined with the turbine condensate in the reactor feed water loop. All of the electricity produced by the NPM was directly supplied to the HTSE block.

The following Figure 3-1 shows a simplified scheme of this plant.

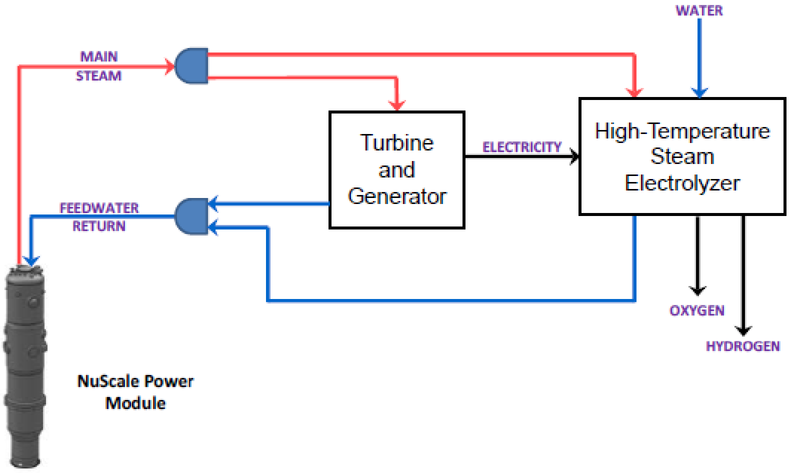


Figure 3-1: Simplified process flow for single NuScale module and HTSE unit hydrogen plant [46]

Since the steam leaving a PWR is approximately at 300 °C, and 800-850 °C are required for the HTSE, a unit that from now on will be called *External Steam SuperHeater (ESSH)* is needed in this case. Indeed, the steam coming from the tertiary loop heats the feedwater (for the HTSE) at least until 290-300°C.

After that a further heating is necessary, that cannot be provided by the NPP, since its temperature is limited (PWR): then ESSH heats the steam until 850 °C, burning a fuel (e.g. natural gas or coal).

While this process sounds very complicated it could reveal interesting. In fact, as is shown in the section 3.4, the most part of the thermal energy needed to heat 30 °C water until 850 °C steam is given in the first part of the heating, where there is the phase transition. So, only a reasonably small part of this energy should be provided by the fuel burnt in the ESSH.

Of course there is a great number of technical issues that should be faced, before realizing a plant like the one just described, but this idea could make accessible the high temperature processes to the cogeneration with LWRs.

Under the (strong) hypothesis that this plant is demonstrated to be technically feasible, this study assesses this coupling from an economic standpoint, and compare the PWR-HTSE coupling to the VHTGR-HTSE one (described in section 2.2.5.3), which is clearly more intuitive (because it does not require any ESSH), but weighted by the weak diffusion of VHTGRs.

The SI cycle is the most promising among all the proposed thermochemical cycles, but it is currently at the first steps of R&D.

Its most interesting property is the necessity of only thermal energy. Again, the coupling with a PWR would require an External Superheater (which would burn some fuel) for the Sulfuric Acid, while the coupling with a VHTGR would not.

As for the Research Output, let us underline again the great difference between AWE, and HTSE and SI cycle: the first one is commercially available (at known costs) with systems of MW-scale which count thousands and thousands of operating hours; the others are very interesting systems for a medium-long term future, but currently not available.

It is intuitive that it makes no sense to perform the same analysis on technologies being at so different levels of their development.

Thus, as for the AWE, in this thesis work the plant is sized, and then it is computed the energy consumptions and the hydrogen production (knowing all the technical data necessary to do it). At this point the economic evaluation of the plant can be performed. Since the Electricity Price reveals to be the key unknown, which determines the profitability of the investment, the aim of the model (research output, section 4.2.1.2) consists in finding the breakeven hydrogen price for each electricity price scenario.

On the other hand, for the HTSE and SI cycle, even the technical data are not completely available (several R&D issues remain open). Furthermore, the main cost (together with electricity cost, which already has been considered unpredictable and so has determined different scenarios), i.e. the capital cost of the plant, is impossible to forecast. Thus a different approach is followed: the aim of this part of the study is to find the breakeven Capital Cost [k€/(mln Nm^3/y) of production capacity] within different scenarios expressed in terms of EP and HP.

Hydrogen Production Method	**T max process**	**Energy Input [kWh/Nm3]**	**Nuclear Reactor**	**Technical feasibility (F) & considerations**	**Economic profitability & considerations**	**Research output**
AWE	80 °C	4.3 kWh Only ELECTRIC ENERGY	SMR PWR	F	Depends on **EE and H2 prices.** All electric sources are the same. **No advantage with SMR**	H2 **breakeven price** for different EE price scenarios
			LR PWR	F		/
			SMR VHTGR	F		/
HTSE	850 °C	2.5 kWh_EL + 0.92 kWh_TH (EE for the most part)	SMR PWR + External Heater	F in theory. ESSH required. **SOEC under R&D**	Uncertain, but increased efficiency and H2 production	**SOEC target Capital Cost**, in different H2 and EE prices scenarios
			LR PWR + External Heater		**Surely LESS profitable** than with SMR [12]	/
			SMR VHTGR	also NPP under R&D	**NO ESSH**. Interesting	SOEC target Capital Cost
SI cycle	850 °C	5.99 kWh Only THERMAL Energy	SMR PWR	F in theory. External Sulfuric Acid SuperHeater required. **SI cyc under R&D**	Further increased efficiency and H2 production	/
			LR PWR		**Surely LESS profitable** than with SMR [12]	/
			SMR VHTGR	also NPP under R&D	**NO ESSH** .	SI cyc target Capital Cost

3.2 Technical aspects of coupling a NPP with an Hydrogen Plant

As already explained, nowadays NPPs follow the grid inserting control rods and neutrons absorbers onto the coolant, then modifying the reactivity within the core.
The idea on which Load Following by Auxiliary Plant is based, consists of leaving the primary loop always work at full nominal (thermal) power rate. Then, during high-load hours (day) the NPP provides at most electric energy to the grid, whereas during low-load hours (night) the not required energy is directed to the auxiliary plant.

Now, the possible industrial plants can be roughly distinct into electrical and non-electrical applications.
In the first case, also the secondary loop, and ultimately the turbine (and so the alternator) work at full load, so the electrical power output is always the plant nominal value. The switch from the grid to the industrial plant will be (conceptually and physically) placed outside of the NPP; therefore no part of the nuclear plant will feel the difference between the two operating modes.
This means that for these applications, there is no difference between SMRs or LRs as electric energy source.
This is the most simple case; no modifications are required to the NPP design, and no physical proximity between the two plants is required. The industrial plant can be placed even several km far from the NPP. This is the case of Water Electrolysis.
In order to operate in the load following mode, the only requirements that the WEP has to meet, is to be large enough to receive all the electric energy not required by the grid during the night, and to be sufficiently flexible to get a great power input during the night, and a very small one during the day.

As for the non-electrical applications, some more observations should be done.
Here, while the primary loop still works at full power, a certain part of the steam flow by-passes the turbine, and runs into a further steam line to an heat exchanger, from which another fluid coming from the auxiliary industrial plant is heated. This means that the secondary loop does meet some modification in terms of thermodynamics conditions at least two times per day (at the beginning and at the end of the night). The turbine will receive a smaller steam flow, and less electrical power will be produced during the night.

In comparison to a NPP in a stand-alone layout, the coupling with auxiliary plants in a cogenerative layout requires some modifications [12]:

1. First of all, the auxiliary plant does not require a boiler or any other kind of source of heat, because the steam comes directly from the nuclear plant;
2. Consequently, O&M costs do not include the purchase of energy, like electricity and natural gas to burn into the boiler;

3. On the other hand, the coupling with a NPP requires an additional heat exchanger and protective barriers (to avoid and prevent potential carry-over of radioactivity to the products) to be installed within the NPP area [132].

Points 1 and 2 lead to a decrease of overnight capital costs and O&M of the plants, whereas point 3 lead to an increase.

Cost of standard IRIS cooling tower condenser, which has to exchange 665 MWt, is assumed 12,5 M$ [133], anyway since it is assumed that the NPP is already built and operating, no costs and no modification in the nuclear plant design are considered.
These values could be taken as reference for the heat exchangers for the coupling between plants, required for the thermal applications (HTSE and SI cycle), considering that the value of heat exchanger in a similar work has been assumed 3-5% of the total overnight capital costs of the corresponding plant [134]; but their costs cannot be calculated simply with the proportional method, because of the peculiarities of the heat transfer required.

More specifically, while the typical nuclear HXs operate al low enthalpy (low temperature process heat), in this case:

- The SOEC plant requires an HX that superheats steam until 850°C [30];
- The SI thermochemical plant requires an HX that superheat *sulfuric acid* until a temperature ranging between 800 and 900°C [30][34].

Since these processes are still under R&D, there is no literature on the HXs that would be necessary for the plants considered in the present study.
Specifically regarding the SI thermochemical plant, there is no data on the possible cost of any component of the system, so it does not make sense to try to calculate the cost of the HX. On the contrary, the capital cost target of the whole plant will be estimated by this study.

As previously said, it is hypothesized that the Nuclear Plant has already been approved, licensed, built and is already operating.
While this is a strong hypothesis, this let focus only on the techno-economic evaluation of the auxiliary plants, without taking into account the 'nuclear part of the investment'.

Table 3-1 lists the principle characteristics of the considered NPPs, which are: an SMR PWR (like, IRIS), and an SMR VHTGR (like, GTHTR300).

LRs are not considered for the coupling, because of the following reasons:

- For the electrical application (AWE) all the technologies (PWR LR, PWR SMR, VHTGR KR, VHTGR SMR, or even a coal or an hydroelectric plant) that are able to provide a constant power of 670 MWe for a certain number of hours per day, are identical from the point of view of the economic analysis of the WE plant;

- For the thermal applications (HTSE and SI cycle) there are relevant differences, that will be focused. However in section 1.1.4.1 it has already been demonstrated that

SMRs suit better the operating conditions that involve the primary loop during the non-electrical cogenerative operation.

Since the starting point of this study, from the nuclear standpoint, is the Load Following with IRIS, all the other considered reactors have been *resized*, in order to make the economic assessment considering equal power reactors, so that they all can provide the same energy to the grid, and to the auxiliary plants, during 1 year, as can be seen in Table 3-1, in which the technical data regarding the NPPs are listed [35], [135].

		PWR: IRIS	VHTGR: GTHTR300	IS unit
Nuclear Power Plant	Thermodynamic efficiency	33.5%	46%	-
	1 SMR nominal Electric Power	335	335	MWe
	Number of SMRs	4	4	-
	NPP nominal Electric Power	1,340	1,340	MWe
	NPP *electric* equivalent available power during the Night	670	670	MWe
	NPP *thermal* equivalent available power during the Night	2,000	1,456	MWth
	Load Factor	95%	95%	-
	Theoretical Annual Electric Energy produced	11,151	11,151	GWh el
	‘Excess Energy’	1,859	1,859	GWh el

Table 3-1: Nuclear Power Plants technical characteristics

Regarding the load factor, for currently operating NPPs it is influenced by the electricity demand from the grid, and it generally ranges between 80 and 90% [9]. Since in this case the NPPs operate in the Load Following strategy, a value of 95% has been taken.

So, since the interest of this study in the nuclear plants is limited on the provided thermal or electric power, the only difference between the two technologies is represented by the TD efficiency, which results in a different quantity of thermal power available, at the same electric power size.

As previously seen, the actual daily power output profile for a Nuclear Plant, varies case by case, strongly depending on the overall energy policy of the considered country, and the power sources present in the proximity of the specific plant taken into exam (see section **Errore. L'origine riferimento non è stata trovata.**).

It is clear that this situation would be too complicated to be studied, so the following simplifications are made:

- the electric power required by grid will be equal to the nominal power during the day (8.00 am to 12.00 pm), and it will be the 50% of the nominal power during the night (0.00 am to 8.00 am);
- this means that the available energy for the auxiliary plant will be 670 MWe (or, in case of thermal application: 2000 MWt with the PWR, 1196 MWt with the VHTGR) for 8 hours;
- all the 365 days of the year are considered identical in terms of energy required by the grid;
- the non-availability days of the NPP, such as the re-fuelling, are taken into account via a capacity factor, that is supposed to be 95%.

3.3 Alkaline Water Electrolysis

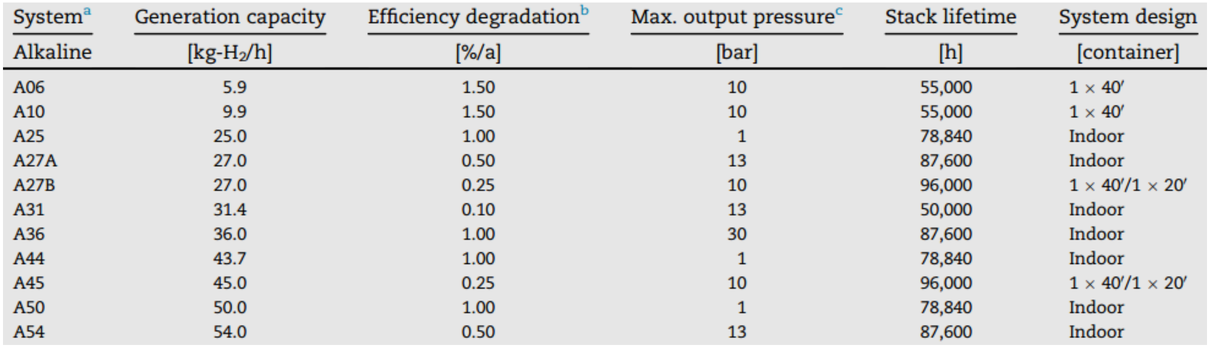
3.3.1 Choice of the Electrolyzer module

As explained in section 2.2.4, alkaline EZs are the most developed and industrially produced, so several EZs manufactures are present in the market.

Sherif et al. [136] explain that the efficiency of an electrolyzer is inversely proportional to the cell potential, which in turn is determined by the current density, and that in turn directly corresponds to the rate of hydrogen production per unit of electrode active area. A higher voltage would result in more hydrogen production, but at a lower efficiency. Typically, cell voltage is selected at about 2 V, but a lower nominal voltage (as low as 1.6 V) may be selected, if the efficiency is more important than size (and capital cost) of the electrolyzer.
Thus, generally a trade-off between efficiency and capital cost has to be achieved.

Given that the Water Electrolysi Plant (WEP) investigated in the present study must be large enough to achieve all the excess power coming from the NPP, it is necessary to deploy a great number of large-scale electrolyzers.

Currently, commercial large-size AEZs have electric power inputs between 0.35 and 3.35 MWe. Felgenhauer et al. [69] present a list of EZs models and essential technical data, noted by mean of a code in order to not disclose the product and company names.

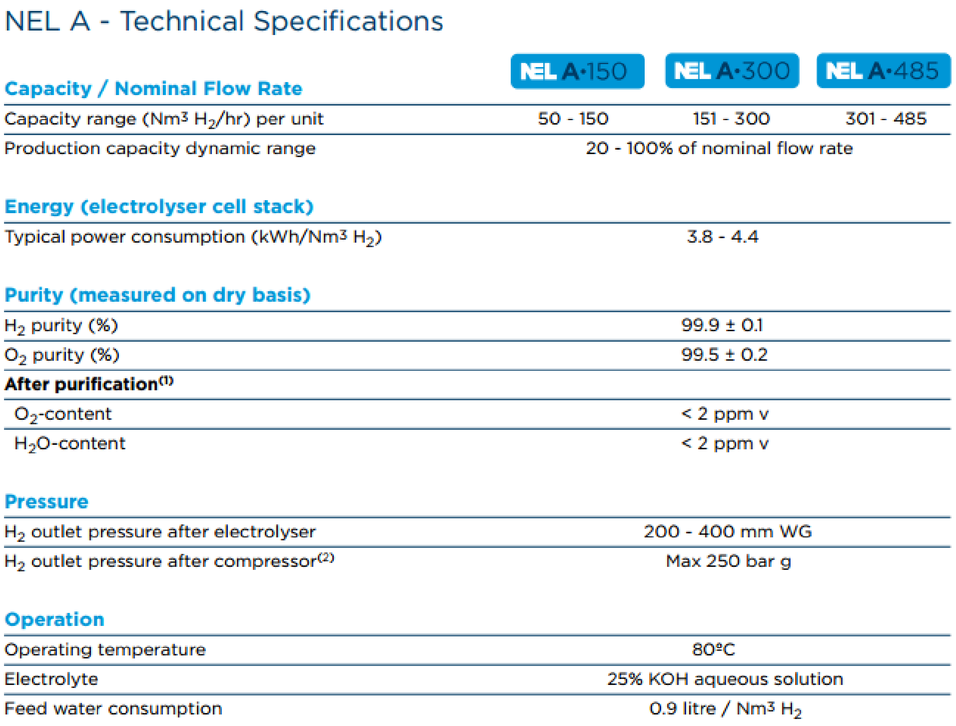


System[a]	Generation capacity	Efficiency degradation[b]	Max. output pressure[c]	Stack lifetime	System design
Alkaline	[kg-H_2/h]	[%/a]	[bar]	[h]	[container]
A06	5.9	1.50	10	55,000	1 × 40′
A10	9.9	1.50	10	55,000	1 × 40′
A25	25.0	1.00	1	78,840	Indoor
A27A	27.0	0.50	13	87,600	Indoor
A27B	27.0	0.25	10	96,000	1 × 40′/1 × 20′
A31	31.4	0.10	13	50,000	Indoor
A36	36.0	1.00	30	87,600	Indoor
A44	43.7	1.00	1	78,840	Indoor
A45	45.0	0.25	10	96,000	1 × 40′/1 × 20′
A50	50.0	1.00	1	78,840	Indoor
A54	54.0	0.50	13	87,600	Indoor

Figure 3-2: Typical technical parameters of a list of available Alkaline Electrolyzers [69]

It can be seen how the efficiency degradation typically ranges between 0.25 to 1.00 %/year, while the stack lifetime ranges between 78,840 to 96,000 hours, with some exceptions(principally for the smallest modules).

After several contacts with the main AEZs manufacturer, a module which represents a good compromise between size (2.2 MWe input) and power consumption (3.8 to 4.4 kWh/Nm^3) has been found. It also have a quite long forecasted stack lifetime, and a relatively low capital cost (see section 4.2.2). This module is the NEL A. 485, produced by NEL Hydrogen [137]. Its technical specifications, that are taken as reference data for the technical analysis, are reported in Figure 3-3.



NEL A - Technical Specifications

Capacity / Nominal Flow Rate	NEL A·150	NEL A·300	NEL A·485
Capacity range (Nm³ H_2/hr) per unit	50 - 150	151 - 300	301 - 485
Production capacity dynamic range	20 - 100% of nominal flow rate		
Energy (electrolyser cell stack)			
Typical power consumption (kWh/Nm³ H_2)	3.8 - 4.4		
Purity (measured on dry basis)			
H_2 purity (%)	99.9 ± 0.1		
O_2 purity (%)	99.5 ± 0.2		
After purification(1)			
O_2-content	< 2 ppm v		
H_2O-content	< 2 ppm v		
Pressure			
H_2 outlet pressure after electrolyser	200 - 400 mm WG		
H_2 outlet pressure after compressor(2)	Max 250 bar g		
Operation			
Operating temperature	80ºC		
Electrolyte	25% KOH aqueous solution		
Feed water consumption	0.9 litre / Nm³ H_2		

Figure 3-3: NEL Hydrogenics Atmospheric Alkaline EZs models technical specifications [137]

Since not all the data regarding the EZ model that are needed for the analysis are available from the catalogue, the missing ones are assumed in line with the ones found in literature [69].

Furthermore some parameters are not exactly sure.

In this case they are taken as the *expected value* of a distribution, of which the minimum and maximum values are also given, so that taking into account the uncertainties (this concept is clarified in section 4.2.1.2 with the best and worst case scenarios, and section 4.2.1.3 with Montecarlo simulations).

The operational input data, including Minimum and Maximum possible value (for uncertain parameters) of the EZ are listed in Table 3-2:

		Expected value	**Min**	**Max**	**IS unit**
Alkaline Electrolyzer (AEZ)	Energy Input per Nm3_H2__year 1	4.3	3.8	4.4	kWh/Nm3
	Efficiency degradation_ Full operation	1.0%	0.7%	1.50%	%/y
	Efficiency degradation_ FR operation	Scenario variable: {2%; 5%; 10%; 20%}	Expected value *90%	Expected value *110%	%/y
	Stack power	2.2	/	/	MW e
	Nominal Generation capacity__Nm3/h	485.0	/	/	Nm3/h
	Stack lifetime	87,600 (10 years)	/	/	h
	Availability hours per year	8,585	/	/	h

Table 3-2: AEZ technical parameters

More specifically:

- The Energy Input (according to the manufacturer ([63] 15., 16.)) varies from 3.8 to 4.4; so assuming 4.3 as expected value is quite conservative. This is the efficiency at the first year of operation. Then the energy required to produce 1 Nm^3 of hydrogen increases year by year, according to the efficiency degradation (see 3.3.4);
- The efficiency degradation is assumed ranging between 0.7 to 1.5 %/year, with an expected value of 1.0 %/year;
- The efficiency degradation under the so called ‘Fast Reserve (FR) Operation’ (see section 3.3.2) is unpredictable, since there are no experiments on this topic. Then, four scenarios which hypothesize different possible values have been investigated;
- After 10 years (according with the forecast of the manufacturer), the excessive degradation of performance requires a replacement of the EZs stacks;
- The availability of the EZs has been assumed of 98%, since the planned maintenance can be effectuated during the daytime, when the EZs operate at low level, with a negligible impact on the production.

3.3.2 Technical needs: dynamics, operating range

In the Load Following operation, a fast dynamic response is actually not required: all the EZ units enter in operation at 0.00 am, work at full load for 8 (or 12) hours, and then are turned to the minimum power level (20%, Figure 3-3); they operate at this level for 16 (or 12) hours, until the next day starts.

Dynamic becomes really essential in the case of the so called ‘Fast Reserve Operation’ (and, secondly in the ‘STOR Operation’), when operating EZs are used in an unconventional way, i.e. as an indirect electrical energy storage.
As already seen, the Reserves enter in operation when the grid has to face a rapid increase of electricity demand. The plant that sells EE in the Reserve market has to be available for the most part of 8760 hours of the year, but are actually on just for a hundred of hours per year.
This market has historically been reserved for technologies that guarantee a very quick response [122]: Pumped Hydro Storage (PHS), Compressed Air Energy Storage, etc.
But, if a NPP is coupled to an operating WE Plant, selling energy on the Reserves market becomes an option. In the next paragraph the functioning of the FR operation is explained, but the STOR operation is in principle the same thing: the only difference, is represented by the number of EZs involved in the operation and the time in which the EZs have to be turned off.

A certain Electric Power (99 MW) is sent to 45 EZs, which operate at full power also during the availability hours (essentially, during the day).
In case of a further electricity request, a certain number of EZs undergoes a rapid shut down, and the electric current is ‘immediately’ (within 2 min) available to the grid.
The main advantage of this method is that *no thermodynamic transient* is required, but only electric. It is almost like moving a current from a mesh to another one via a switch.
When the grid does not require the reserve power anymore, the power is again sent to the EZs that return in operation.

Before finding out if this hypothesis is economically profitable, the technical feasibility has to be verified.
The key issue for the feasibility is that the dynamics of the EZ has to meet the requested standards of Fast Reserves, which are the most constraining.
The FRs power source must guarantee [124]:

- Available power from 0 to 50 MW within 2 minutes and for at least 15 min;
- With an increasing power range of 25 MW/min.

At this point the questions are: are the EZs capable of this? What consequences on the produced hydrogen quality and on the efficiency degradation could cause this operation mode?

Now, there is no experiment experience in the rapid shut down of EZs, and no model that can predict the EZ response is available.

Nevertheless, it has been tried to answer this question following two different paths:

- Scientific literature concerning widely variable power input to EZs has been studied;
- Moreover several academic experts and companies in the EZ field have been asked an opinion about this matter;

As for the literature, the variable power input to EZs is deeply treated in the analysis of the hydrogen production via wind power or PV, in order to store energy.

In particular, [138] examines the effects of fluctuating power supplies on electrolyser operation. Their experiments have been performed on two alkaline EZs belonging to the kW scale, which underwent an intermittent operation, characterized by alternate overload, partial load, shut-off and dynamic periods, such as the one represented in Figure 3-4.

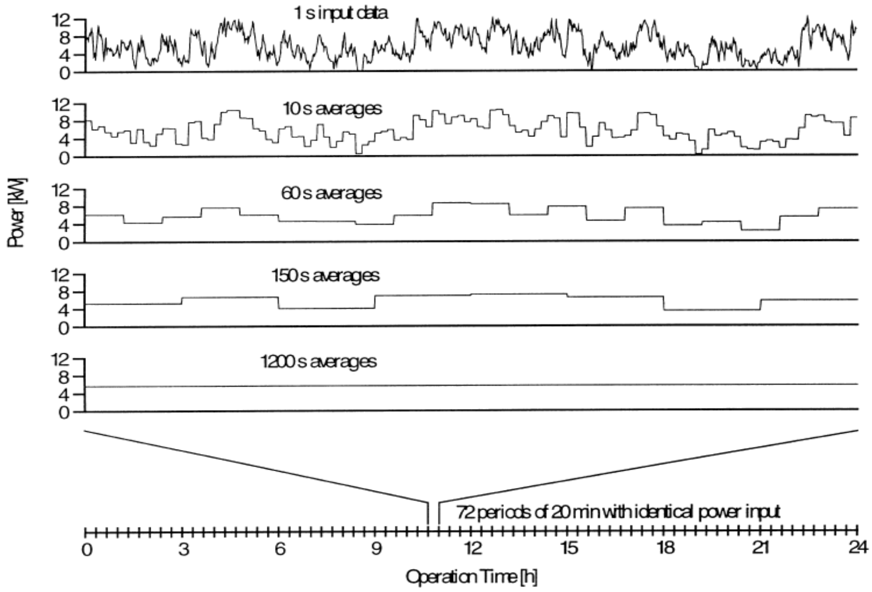


Figure 3-4: Power time series input for dynamic investigation of electrolyser response [138]

The main effects of this treatment are:

- changes in gas production, due to rapid load fluctuation, that causes level changes in the gas separating vessels, which in turn promote diffusion processes inside the cell, that result in reduced purity of the product gases.
  Indeed at very low loads, the rate at which H_2 and O_2 are produced, becomes lower than the rate at which the gases permeate through the electrolyte and mix with each other [136].
  It is also worth saying that low purity output gases might be particularly dangerous on the oxygen side: if the safety limit (2 vol.% of H_2 in O_2) is exceeded, the electrolyser is automatically shut down;

- with regard to short term operation, power fluctuations have no significant effect on the overall electrical stability of the electrolyser;
- the reduction of efficiency due to variable load factor operation is limited to a few per cent;
- high impurity levels of H_2 in O_2 during operation at low current and after some hours of stand-by operation might be detected. These are principally due to gas leaks from pipe connections and to an insufficient insulation of the anode. It has been demonstrated that these inconveniences can be solved with an improved design of the EZ and a better materials choice.

According to [136], thermal management could also become a problem with an highly variable power source. Since the EZ takes time to reach its normal operating temperature, frequently varying the load could cause it to work on average at a lower temperature, which leads to a lower efficiency.

As for the shut-down required time, which plays an essential role in the STOR (Short Term Operating Reserves) and the FR (Fast Reserves) operation, either academic researchers ([63] 12., 13., 20.) in the field of Alkaline EZs and EZs manufacturers ([63] 14., 16.) agree that it can be done within 2 minutes, without damaging the system. More or less the same time is needed by the EZ to enter in operation.

After all, it seems plausible that an alkaline EZ meet the requirement of a FR power source (which is the most stringent, for the EZ), with an efficiency loss and degradation that is not possible to quantify without performing specific experiments ([63] 12., 13., 20.).
Since a forecast is not possible, different scenarios of the EZ response under these exceptional operations will be considered.

3.3.3 Sizing the WEP

Once the available electric power from the NPP is fixed, and the EZ model is chosen, it results immediate to size the WE plant.

		Expected value	IS unit
WE INPUT Power	No. Stack	304	-
	WE plant size	669	MWe
	EZ Night Operation Load	100%	-
	EZ minimum operation Load	20%	-

Table 3-3: Water Electrolysis Plant power input parameters

Since the available power from the NPP is approximately 670 MW, 304 EZ units are supposed to be installed, for a power input of 669 MW.

During the night, all the EZs operate at the maximum operation load. As for the day, for the priority is to sell electricity, it would be desirable to send 0 MW to the WEP.

According to the manufacturer ([63] 15.,16.), since it is not possible to protect the cathodes during the day by flushing all the system with nitrogen (this is made only for stops which last much more than some hours), there remains two options:

- the *stand-by mode,* during which the lye pump is kept in operation (with a negligible power consumption) to maintain the electrolyte circulating. As long as the temperature of the electrolyte does not drop too much, there is not a need to insert inert gas. Anyway in this case a significant increase of the degradation is expected;
- the minimum load mode: during the daytime the EZ continues to operate at 20% of its nominal capacity, preserving the electrodes.

Finally, the second option has been chosen, in order to avoid an unpredictable degradation of the electrodes.

For an Electrolyzer the size is commonly expressed by its power input, in place of its hydrogen production technologies, it is necessary to express all the sizes in terms of the capacity of *output*, since different technologies imply different efficiencies.

For the WEP the Plant Capacity is simply obtained multiplying the nominal generation capacity of 1EZ by the number of EZs:

$$\boldsymbol{WEP\ Plant\ Size = 147.44\ [kilo\ \frac{Nm^3}{h}]}$$

3.3.4 WEP annual production

Different operating options have been considered for the Water Electrolysis Plant.

First of all, as can be seen in Table 3-4, for each operating mode, listed in the first column, Day and Night Operation (column 2) are treated separately. Conventionally, this work refers to ‘Day Operation’ as the hours with greater demand for electricity, and ‘Night Operation’ as the hours with the lower one.

During the ‘Day Operation’ selling electricity is the priority, and so the EZs work at the minimum load.

In the third column it is presented the product: Electric Energy to grid (for the day ahead market) and Hydrogen from the WEP are the only product of the ‘pure’ LF; then, the cases considering the ‘STOR’ and ‘Fast Reserve operation’ are presented. Here, a third product is added: the electricity sold as reserve (EE sold as STOR, and as FR, respectively).

Case description	Time	Product	MW input	Hours per day	Hours per year
Base Case 8 (BC 8): Load Following only (8 h night)	Day	EE	1,206	16	5,548
		H_2	134		
	Night	EE	671	8	2,746
		H_2	669		
Base Case 12 (BC 12): Load Following only (12 h night)	Day	EE	1,206	12	4,119
		H_2	134		
	Night	EE	671	12	4,119
		H_2	669		
STOR operation (STOR): 55 MW allocated to STOR (day only)	Day	EE	1,162	16	5,548
		H_2	134		
		H_2 in 'ready state'	55	10.6	3,634
		EE as STOR	55	0.2	78
	Night	EE	671	8	2,746
		H_2	669		
FR operation (FR): 99 MW allocated to FR (day only)	Day	EE	1,127	16	3,972
		H_2	134		
		H_2 in 'ready state'	99	11.6	4,223
		EE as FR	99	1	365
	Night	EE	671	8	2,746
		H_2	669		

Table 3-4: WEP operating modes inputs description

Let us initially focus on the Base Cases: BC 8 and BC 12. In the Base Case only 'pure' Load Following is performed, so the total power go to the grid during the day, while half of it (679 MWe) goes to the WEP during the night.

Even though assuming that the electricity demand from the grid is steady for all the day, and then jumps to 50% at a certain time is a strong simplification, the demand decrease during the night actually lasts more or less 8 hours, so this value is generally assumed for the LF [13], because it is the best from the grid standpoint.

Anyway it is also investigated a LF mode in which the WEP works for 12 hours per day.
The BC 12 is in principle identical to BC 8, with the only difference figured by the total amount of energy used by the WEP during the day, which means more produced hydrogen, but also a greater electricity cost.

Moreover, two other operating modes have been considered in this thesis work, for the Water Electrolysis Plant: the so called 'Short Term Operating Reserves' and 'Fast Reserves' modes.
One of the aims of this research study is to understand if combining the AWE to the Reserve services can provide a significant extra-value to the investment.

It should be noticed that as for the Night Operation, the STOR and FR are identical to BC 8. The only difference lies in the Day Operation.
The STOR and FR operation are described as follows:

- STOR operation: in this case 55 MW have to be available for 3864 h/y (that is 10.6 hours per day, average) for the STOR electricity market, so this power is delivered to the EZs during this time. This implies that the electric power made available for the grid (day ahead) during Day Operation is 1,162 MW (=1,340–55—power for 20% load of other EZs).
  Since 55 Mw are necessary, only 25 EZs over 304 are involved in this operation, the others operate at 20% for all the day.
  Just for 78 hours per year (0.2 h/d) the EZs are shut down and the EE is actually sold on the STOR market.
- FR operation: in this case 99 MW have to be available for the FR electricity market, so 45 EZs are involved in the FR Day Operation . The availability periods are longer than for STOR. As can be seen from [139], the required availability varies from tender by tender, but generally it is 12 h during the weekdays, and around 10 h during the weekends or bank holidays [124], so the availability hours per year are approximately 4,223.
  It is very difficult to forecast the quantity of EE that will actually be sold on the FR market during a year, since the contracts refer to a maximum value of utilisation. So the revenues coming from the FR are computed as maximal values.
  A typical contract assigned to Scottish Power Generation [139] provides a limit of 30 min per settlement period (i.e. from 6.00 am to 10.30 am): which roughly means 1 hour per day at full power.

Once the technical data of the EZ model have been presented, the whole WEP has been sized, and the electric power distribution between the grid and the WEP for all the operation modes has been described, it results very simple to calculate the annual hydrogen production for each operation mode.

For instance, here it is presented the calculation of the first year production during the Night Operation in the BC 8. The other cases are treated in the same way. Since the Electric Power input, P_{WE}, and the operating hours are known, the production is:

$$EE_{y1} = P_{WE} * h_{op} = 669[MW] * 2{,}746[h] \approx 1{,}843\ [GWh]$$

$$H_{2,prod\ y1}\,[mln\ Nm^3] = \frac{EE_{y1}}{W_{real}} = \frac{1{,}843[GWh]}{4.3\ \left[\frac{kWh}{Nm^3}\right]} \approx 428.6\ [mln\ Nm^3]$$

This procedure let obtain the production for the first year. Then, since the complex phenomenon of the efficiency degradation begins to take place, the W_{real} (that is the real electric energy required to produce 1 Nm^3_{H2}) increases. This process leads to a progressive reduction of the hydrogen production.

Coherently with the data found in literature [69], referred to several models of EZs, an expected value of efficiency degradation rate of 1%/y in terms of LHV is taken, even though this is probability a pessimistic assumption.
In order to simplify the model, it is assumed that the efficiency decreases with a constant rate, which is not necessarily true.
Then, the W_{real} at the n-th year, can be computed as follows:

$$W_{real\,,i} = \frac{LHV}{\varepsilon_i}$$

$$W_{real\,,n} = \frac{W_{real,1}}{(1-\varepsilon d)^{n-1}}$$

After 10 years, the W_{real} decreases from 4.3 to 4.7, which implies a decrease in hydrogen production from 429 to 392 $mlnNm^3$.

This effect of production decrease is taken into account calculating the revenues based on the average production over 10 years. At the 11-th year, the EZs stacks are supposed to be replaced with new ones. This is a simplification too: actually some EZs will fail after 5 or 6 years of operation, and some will survive beyond 10 years. Working with a so large number o system, a more or less continuous regeneration of the stack is expected, so making the computation taking average values is enough precise.

A different treatment is reserved to the FR operation. Indeed, while in the STOR operation the 25 EZs that work also during the day are not affected by a relevant difference in their degradation, this is not the case of FR operation, where the 45 EZs that work also during the day are often turned on and shut-down several times (from 5 to 10) per day.
The effect of this use on the EZ's efficiency is not predictable, but according both to manufacturers and academics essentially the degradation would be surely faster: only specific experiments can verify if quite faster or catastrophically faster.

So, in order to mitigate the uncertainty, different scenarios for the FR operation are considered, in which the efficiency degradation rate varies from 2 to 20 %/year.

In **Errore. L'origine riferimento non è stata trovata.** all the operation modes inputs are reviewed, and outputs (hydrogen production and sold electricity) are added. As for the FR production, just one representative output (the median value, between all the considered efficiency degradation) has been inserted in the table.

Case description	Time	Product	MW input	Hours per day	Hours per year	Annual Output	IS unit
Base Case 8 (BC 8): Load Following only (8 h night)	Day	EE	1,206	16	5,548	7,097	GWh
		H_2	134			74.9	Mln Nm^3
	Night	EE	671	8	2,746	1,843	GWh
		H_2	669			408.1	Mln Nm^3
Base Case 12 (BC 12): Load Following only (12 h night)	Day	EE	1,206	12	4,119	5,270	GWh
		H_2	134			55.6	Mln Nm^3
	Night	EE	671	12	4,119	2,765	GWh
		H_2	669			612.1	Mln Nm^3
STOR operation (STOR): 55 MW allocated to STOR (day only)	Day	EE	1,162	16	5,548	6,897	GWh
		H_2	134			68.8	Mln Nm^3
		H_2 in 'ready state'	55	10.6	3,634	44.4	Mln Nm^3
		EE as STOR	55	0.2	78	4.29	GWh
	Night	EE	671	8	2,746	1,843	GWh
		H_2	669			408.1	Mln Nm^3
FR operation (FR): 99 MW allocated to FR (day only)	Day	EE	1,127	16	3,972	6,703	GWh
		H_2	134			63.6	Mln Nm^3
		H_2 in 'ready state'	99	10.5	4,223	87.4	Mln Nm^3
		EE as FR	99	1	365	36.14	GWh
	Night	EE	671	8	2,746	1,843	GWh
		H_2	669			408.1	Mln Nm^3

Table 3-5: WEP power input, operating hours and annual production for all the operating modes

Finally, it is necessary to calculate the annual not-sold electricity, which represents the electricity cost of the WEP.

Case description	Time	Not Sold Electricity [GWh]
Base Case 8	Day	4,054
	Night	9,308
Base Case 12	Day	5,881
	Night	8,386
STOR	Day	4,254
	Night	9,308
FR	Day	4,448
	Night	9,308

Table 3-6: Not Sold Electricity for all the operating modes

Now, the WEP size, the annual required EE, and the consequent H_2 production for each operation mode are known. This closes the technical analysis of the Water Electrolysis Plant. In the next chapter, these data will be inputs economic model, in order to compute the capital and annual costs and the revenues.

3.4 High Temperature Steam Electrolysis Plant

3.4.1 HTSE - Sizing

In the 2.2.5.2.4 section the R&D open issues regarding the SOECs have been exposed, so it is clear how in this case it is impossible to choose a SOEC model, with definite technical parameters and cost, to perform an economic analysis.

A different kind of plant sizing is made in this section:

1. From the Figure 2-17 is deduced the (theoretical) required energy, both electric and thermal, to produce 1 Nm^3 (and 1 kg) of H_2: approximately 2.5 kWh_el and 0.9 kWh_th per Nm^3;

2. The Electric Power is supplied directly to the SOEC, to let the electrochemical reaction take place. The heating process from 30°C water to 850°C steam is studied from the energy balance point of view.
   In particular, the couplings with a PWR and a VHTGR (whose characteristics are listed in Table 3-1) are considered; while the VHTGR can raise the water temperature until 850 °C by itself, the heating made by PWR outcoming steam can reach at maximum 290°C, approximately.
   Then, the further heat must be provided by another energy source (in this study, Natural Gas) into the External Heat SuperHeater (ESSH). So in the PWR case, just a *part* of the required thermal energy is provided by the NPP. The operating pressure is supposed to be 35 bar, according to the data present in literature [34], [68], even though different operating pressures are possbible.
   In Table 3-7 are listed the TD relevant points of the heating process:

Temperature [°C]	Entalpy_phase (symbol)	Value [kJ/kg_H2O]
30	h_liq_30	129
240	h_liq_240	1,037
245	h_steam_245	2,811
290	h_steam_290	2,949
850	h_steam_850	4,263

Table 3-7: Thermodynamically relevant points for the water heating process in HTSE

It can be noticed that between 240 and 245°C there is the transition of phase, so the enthalpy increases of 1.8 MJ/kg within 5 degrees.

The thermal energy input for the water heating is 4,263—129 = 4,134 kJ/kg_H_2O.
Now, it should be reminded that considering the molecular weight of the water and atomic weight of the hydrogen, it needs 9 kg_H_2O to obtain 1 kg_ H_2.
So the thermal energy input definitely is 37.2 MJ/kg_ H_2.

It is simple to verify that heating from 30 to 290°C (this part of the heating will be called from now on: Low Temperature Heating, LTH) requires approximately the 68% of total thermal energy, while the part from 290 to 850 °C (High Temperature Heating, HTH) is the 32%.

If converted in kWh/Nm^3 units, the LTH and HTH are, respectively:

Item	Value [kWh_th/Nm^3]
LTH	0.63
HTH	0.29

Table 3-8: Low and High Temperature water Heating in HTSE

Now, going back to the coupling with the reactors, it is possible to calculate the amount of thermal energy that the NPP and the Burning Gas Plant supply to the SOEC:

	Kind of energy	PWR + NG	VHTGR
From NPP	Thermal	0.63 kWh/Nm^3	0.63+0.29= 0.92 kWh/Nm^3
	Electric	2.5 kWh/Nm^3	2.5 kWh/Nm^3
From NG	Thermal	0.29 kWh/Nm^3	0 kWh/Nm^3

Table 3-9: Nuclear and Natural Gas energy contribution to water heating in HTSE

3. The last step, in order to calculate the size of the HTSE plant is to merge the available power from the NPPs and the energy required by the HTSE process.
   The available power in all the cases is 670 MWe, i.e. the half of the NPP power output.
   Given that the TD efficiencies of the PWR and VHTGR are not the same, for the same available electric power, different quantities of thermal equivalent power are available.
   For each NPP, a different combination of the thermal and electric power must be found, because:

   - The total thermal equivalent power is not the same (see Table 3-1);
   - The ratio between thermal and electric power required is not the same, since in the PWR case, part of the thermal power is supplied by the Natural Gas burner (also called ESSH).

Finally, the right combination is obtained by mean of a goal seek, and the results are:

	Kind of power	**PWR + NG**	**VHTGR**
From NPP	Thermal	156 MWth	211 MWth
	Electric	618 MWe	573 MWe
From NG	Thermal	72 MWth	0 MWth

Table 3-10: Nuclear and Gas Turbine power contribution to HTSE process

4. As for the SOEC, a size of 2 MWe input is hypothesized, so the number of SOEC modules is:

$$SOEC\ modules = \frac{Total\ Required\ Electric\ Power}{SOEC\ power\ input}$$

Finally the size of the HTSE plant (in terms of production capacity) is simply computed as the ratio between the Electric Power offered by each NPP and the electric energy required by the process (from Table 3-9 and Table 3-10).

$$\boldsymbol{HTSE\ Plant\ Size} = \frac{Electric\ \ Power\ \ Input}{Electric\ \ Energy\ \ required} = \frac{618\ \ \mathrm{MW}}{2.5\ \ \frac{kW\,h}{Nm^{\,3}}} = \mathbf{247.2}\ \left[\frac{\boldsymbol{kilo\ Nm^3}}{\boldsymbol{h}}\right](\boldsymbol{PWR}+\boldsymbol{NG})$$

The results for the two couplings, are listed in Table 3-11:

	PWR + NG	**VHTGR**
# SOEC modules	309	287
HTSE Plant Size [kilo Nm^3/h]	247.2	229.6

Table 3-11: HTSE Plant Size according to the coupling with the NPP (PWR+NG and VHTGR cases)

3.4.2 HTSE annual production

Starting from the plant size it is easy to calculate the annual production. A BC 8 operation mode (8 hours of full operation during the night, and 16 hours at a minimum operating level during the day) is supposed to be adopted.

The hourly production is computed in the same way for the AWE, as the ratio between Electric Power and efficiency (see 3.3.4). In this case the efficiency is much superior than the one of AWE, but since the efficiency degradation (EfD) is one of the most serious problems affecting the SOEC, different scenarios about the EfD values have been considered: {2%/y; 5%/y; 10%/y; 20%/y}, and this leads to different productions.

The technical inputs are listed in Table 3-12
For the HTSE, only a deterministic analysis is performed.

		Expected value	**IS unit**
Solid Oxide Electrolyser Cell (SOEC)	**Electric Energy Input per Nm3_ year 1**	2.5	kWh/Nm3
	Efficiency (LHV)__year 1	119%	-
	Efficiency degradation: scenario variable	{2%;5%;10%;20%}	%/y
	Stack power	2	MWe
	Nominal Generation capacity__Nm3/h	800	Nm3/h
	Stack lifetime	Unpredictable: dependent variable	h
	Availability hours per year	8,585	h
	Operating range (day/night)	20—100%	

Table 3-12: SOEC model technical parameters

One could be surprised to see an efficiency exceeding 100%, but this is due to the definition of efficiency in the case of water/steam electrolysis: it is the ratio between the energy output in terms of hydrogen LHV and the *electric* energy input (the thermal energy input is not taken into account). Since the LHV of 1 Nm^3 of hydrogen is 3.3 kWh (see Figure 2-7), the efficiency of the HTSE is in some way superior to 1 (but clearly if the thermal energy is added the sum overcomes the LHV).
The stack lifetime depends on the efficiency degradation presented by the SOEC model.

Different degradations present different stack lifes, which implies different Stack replacement costs.

The power inputs (electrical, and thermal) from each source (PWR and NG) to the HTSE plant are presented in Table 3-13, then the annual production can be computed. The results are presented in Table 3-13, which has the same structure of Table 3-5, where the results of the production of the WEP are shown.

Case description	Time	Power Source	Product	MW input	Hours per day	Hours per year	Yearly outputs	Unit of measure
PWR + NG	Day	NPP	EE to grid	1,206	16	5840	7,043	GWh_el
			EE to HTSE	124			289	Mln Nm^3
			TE to HTSE	31				
		NG	TE from NG	14				
PWR + NG	Night	NPP	EE to grid	670	8	2920	1,956	GWh_el
			EE to HTSE	618			772	Mln Nm^3
			TE to HTSE	156				
		NG	TE from NG	72				
VHTGR	Day	NPP	EE to grid	1,206	16	5840	7,043	GWh_el
			EE to HTSE	115			268	Mln Nm^3
			TE to HTSE	42				
		NG	TE from NG	0				
VHTGR	Night	NPP	EE to grid	670	8	2920	1,956	GWh_el
			EE to HTSE	573			669	Mln Nm^3
			TE to HTSE	211				
		NG	TE from NG	0				

Table 3-13: HTSE Plant power inputs, operating hours and annual production.

It should be noticed that most of the energy provided by the NPP is electricity: compared with the WEP the electric power decreases from 669 only to 618 MW, so it is not really appropriate to refear to HTSE as a thermal application. Anyway it can be consider very attractive due to its great overall efficiency.

The last step: the energy consumption from the NPP, electrical and thermal is used to compute the total Not Sold Electricity, shown in Table 3-14. As for the Thermal Energy, the Electricity that would have been generated from it is taken into account.

Case description	Time	Not Sold Electricity [GWh]
PWR + NG	Day	783
	Night	3,913
VHTGR	Day	783
	Night	3,913

Table 3-14: HTSE Plant Not Sold Electricity

This concludes the technical analysis of the HTSE plant.

3.5 Sulfur-Iodine cycle Termochemical Plant

3.5.1 SI cycle – Sizing

All the considerations about uncertainties on technical parameters that have been made on the SOEC are still valid for this hypothetical plant.

The plant sizing follows essentially the same principle and steps, with the simplification due to the request of thermal power only, by the SI cycle.

The enthalpy variation per mol of hydrogen produced in the two endothermic reactions, with the related enthalpy variations, are listed in Table 3-15 [30]:

Reaction	Temperature [°C]	Enthalpy variation (symbol)	Enthalpy variation value [kJ/mol_H$_2$]
$H_2SO_{4(aq)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \frac{1}{2}O_{2(g)}$	900°C	ΔH_{II}	325.4
$2HI_{(aq)} \rightarrow H_{2(g)} + I_{2(g)}$	450°C	ΔH_{III}	157.8

Table 3-15: Enthalpy variation for the chemical reactions of the SI cycle

If the two values are summed and converted to kWh/Nm^3, according to:

- The Avogadro law: approximately 22.4 liters within 1 mol, in standard temperature and pressure conditions;
- The equivalence 1 m^3 = 1,000 liters;
- The equivalence 1 kWh = 3,600 kJ.

The thermal energy input for the SI cycle is obtained:

$$\mathbf{Thermal\ Energy\ Input} = \mathbf{5.99}\ [\mathbf{kWh_{th}/Nm^3}]$$

From the NPP side, again two solution are considered: PWR+NG and VHTGR.
The available thermal power from the NPPs are simply computed: both provide the thermal power equivalent to the 670 MWe not required by the grid; so the TD efficiency represents the difference. The available thermal power are:

from PWR	from VHTGR
1,997 MWth	1,454 MWth

Due to its higher thermal efficiency, the VHTGR produces the same 670 MWe with less thermal power than PWR, thus it also has less power available for the SI Plant.

In this case it is far more difficult to estimate the share of the thermal energy input that a PWR (with its capability of heating up to 290 °C) could cover, since not only water is involved in the process.
Anyway it should be noticed that with the (strong) assumption that the PWR can cover approximately the 66% of the energy input, an External Heater of approximately 1,000 MW would be required (for the HTSE an external heater of just 72 MW has been hypothesized).
This suggest to give up the idea of coupling the SI Plant with a PWR+NG system, and investigate only the VHTGR.
At this point, in order to size the SI Plant, the ratio between the available thermal power and the energy input is made:

$$\boldsymbol{SI\ Plant\ Size} = \frac{Thermal\ \ Power\ \ Input}{Electric\ \ Energy\ \ required} = \frac{1{,}454\ \ \mathrm{MW}}{5.99\ \frac{kW\,h}{Nm^3}} = \mathbf{242.7}\ \left[\frac{\boldsymbol{kilo\,Nm^3}}{\boldsymbol{h}}\right]$$

3.5.2 SI cycle – Annual production

Starting from the plant size it is easy to calculate the annual production. Again a BC 8 operation mode is supposed to be adopted.

The hourly production is computed by mean of a simple proportion. During the night a 100% of load factor is considered, thus the hourly production is the nominal capacity of the plant.

The question if a SI Plant would be flexible enough to perform Load Following is serious and not-easy to answer. Realistically, this plant would present all the problems of thermal inertia and low flexibility which generally characterize large thermochemical plants. However, for now the process is under R&D and there are not enough information neither to confirm or deny these suppositions.

As it regards the scope of this thesis, subject to the above comments, a load factor of 20% has been assumed for the daytime operation; thus the hourly production during the day is simply the 20% of the Plant Size: i.e. approximately 40 kilo Nm^3/h.

It is not found in the literature a particular process that results in a degradation of efficiency; thusthe variable scenario that captures the uncertainty regarding the level acquired by technology, will be represented by the O&M cost (see4.4.2).

The technical inputs are listed in Table 3-16.
Also for the SI Plant, only a deterministic analysis is performed.

		Expected value	IS unit
Sulfur-Iodine Plant	Thermal Energy Input per Nm3	5.99	kWh/Nm3
	Input power	1,545	MWe
	Nominal Generation capacity__Nm3/h	242,700	Nm3/h
	Plant life	20	y
	Availability hours per year	7,008 (80%)	h
	Operating range (day/night)	20—100%	-

Table 3-16: Sulfur-Iodine Plant model technical parameters

The power inputs to the SI plant are presented in Table 3-17Table 3-13, then the annual production can be computed. The results are presented in Table 3-17, which has the same structure of Table 3-5, where the results of the production of the WEP are shown.

Time	Product	MW input	Hours per day	Hours per year	Yearly outputs	Unit of measure
Day	EE to grid	1,206	16	5840	7,043	GWh_el
	TE to SI	291			227	Mln Nm^3
Night	EE to grid	671	8	2920	1,956	GWh_el
	TE to SI	1,454			567	Mln Nm^3

Table 3-17: SI Plant power inputs, operating hours and annual production

It should be noticed that the electric energy provided to the grid, is the same in all the cases, but the production achieved by the SI Plant is much larger than the one of the AWE.

The last step: the total Not Sold Electricity, is again the same of the WEP BC 8 and of the HTSE.

Time	Not Sold Electricity [GWh]
Day	783
Night	3,913

Table 3-18: SI Plant Not Sold Electricity

This concludes the technical analysis of the SI plant.

4 Economic analysis

4.1 The Discounted Cash Flow method

4.1.1 Deterministic analysis

In capital budgeting the traditional methods are based on the Discounted Cash Flow (DCF) analysis framework, that is an investment valuation methodology focused on the *time value* of money. There are literally hundreds of DCF models, but they all based on the same foundation that simply involves calculation of the Net Present Value (NPV) of a project over the entire life cycle (say T, e.g. 20 years), accounting for the investment costs and the production phase free cash flows.

The method that financial analysts use to value projects may range from the simple to the sophisticated, but the building blocks are the same. Any valuation starts with estimation of costs and revenues over the project life. Because of the time value of money, each cash flow from the future is converted into today's value, using the formula:

$$PV_t = \frac{FV_t}{(1+r)^t}$$

where FV is the future value of the cash flow, PV is the present value, r is the discount rate per time period, and t is the number of the time period.

The project NPV is simply the summation of the PVs of all the cash inflows and cash outflows:

$$NPV = \sum_t PV_t = \sum_t \frac{FV_t}{(1+r)^t}$$

Then the optimal investment rule is to proceed with a project if its NPV is greater than zero and, in case of a portfolio with two or more different projects, the priority will be given to that one with the larger NPV [140].

Another famous decision parameter that belongs to the DCF approach is the Internal Rate of Return (IRR). This profitability indicator is the discount rate at which the NPV became equal to zero. Greater is the IRR of a project, more attractive is the investment.

In the energy field, one more DCF based method is the Levelised Cost of Electricity (LCOE) approach, that allows to compare the costs, per energy produced, of different energy supply technologies. It is for example useful for an investor that has to decide between a nuclear power plant and a CCGT (Combined Cycle Gas Turbine), or between different projects for two or more SMRs. LCOE is calculated in this way:

$$LCOE = \frac{\sum_t \frac{R_t}{(1+r)^t}}{\sum_t \frac{E_t}{(1+r)^t}}$$

where R_t is the expenditure at time t (including investments, O&M, waste disposal, fuel costs, and so on) and E_t is the amount of electricity produced at time t.
As it is clear from the equations, the discount rate is a fundamental parameter to determine for the analysis. It can modify the final decision about an investment, because it directly changes the NPV. Actually, the meaning of the discount rate is the rate that is used to convert the future value of the project cash flow to the present value. It is adjusted for the risk perceived to be associated with the project: the higher the risk, the higher the discount rate. Indeed, business is basically about taking *risks*. The higher the risk and the higher the returns that investors will expect. In the finance world, risks are broadly classified as market risks and private risks. To give a rough definition, it is generally accepted that risks that can be captured in the value of a traded security are *market risks* and all the other are *private risks* [141].

Thus, one of the biggest dilemmas an investor faces is what discount rate to use in the NPV calculations. If there is not uncertainty at all on a cash flow stream, the appropriate discount rate is a *risk-free rate*. If there is uncertainty, the next consideration is whether the stream is influenced by market or private risk. If it influenced by private risk, the investor will not pay a risk premium for the ineptness of the organization in completing the project or the ineffectiveness of the technology involved. On the other hand, if the cash flow is subject to market risk, one would account for it in some fashion, mostly common by adjusting the discount rate. Actually, in the real world it is difficult to completely separate the private risk from market risk. Furthermore any project investments requires capital, and organizations have to pay a cost to obtain capital. Therefore for discounting the cash flows that are subject to private risk, practitioners use a rate that is ether slightly higher than the risk free rate or a rate that is commensurate with the organization's *weighted average cost of capital (WACC)*. It is calculated in the following way:

$$WACC = W_d C_d * (1 - tax) + W_e C_e$$

where W_d and W_d represent how the stakeholders share the financing of an investment. The subscript *d* stays for debt, while the subscript *e* stays for equity. Cost of capital represents the cost of financing an organization's activities, which is normally done through some combination of debt and equity. The debt includes banks, financing agencies, public investments and so on. Their gains are predefined by contract and they have the priority for the investment recovery. On the other hand, the equity represents shareholders in general. Their investment is more flexible and risky because they don't have the priority for the investment recovery and their remuneration is not guaranteed, especially in case of bankruptcy. For these reasons, the cost of equity (C_e) is higher in comparison with the cost of debt (C_d). WACC can be used as a proxy to represent the private risks related to project investments cost. Costs of capital are the rate expected by the banker (interests) or by the investor (returns).
Therefore, the DCF methodology, although is simple and easy to implement, presents three substantial criticalities:

1. The discussed choice of the discount rate;
2. The weak consideration of stochastic nature of the cash flows: DCF cannot capture any market uncertainties, like electricity and fuel prices, or technical uncertainties, like construction costs that vary considerably along construction time [142];
3. The assumed passivity of the management, unable to improve the results after the resolution of some uncertainties [143].

In order to overcome to the problems of uncertainties, after having evaluated our investment by mean of the Deterministic DCF method, this study performs a Montecarlo analysis: probability distributions are associated to those variables (either technical and economic) that are not considered sure, so that the output itself is a probability distribution.

4.1.2 Montecarlo analysis

The calculation of the NPV is based on a set of fixed assumptions related to the project payoff (a deterministic approach), whereas the payoff is uncertain and probabilistic.

The Monte Carlo (MC) simulation is based on the idea that simulating state variables' trajectories can approximate probability distribution of terminal asset values. For every simulation, a defined number of paths is generated, sampling the values of the stochastic processes. Since it is computationally heavy, it is indicated for complex cases with many sources of uncertainty.

In this study there are many variables that can bring to positive or negative NPV. They are for example the prices of the products involved: electricity and hydrogen. Moreover, even the costs of the plants can represent a source of uncertainty, and the O&M costs that affects the annual cash flows, as well.

Because of the great complexity that surrounds the decision about the investment in such a plants, in this study Monte Carlo simulations have been used to simulate the following uncertainties:

- Price of electricity;
- Price of hydrogen;
- Efficiency of the Electrolyser;
- Efficiency degradation of the Electrolyser during *'standard'* operation (i.e. BC 8, BC 12 and STOR, where EZs are not particularly put on strain);
- Efficiency degradation of the Electrolyser during *Fast Reserve* operation;
- Capital Cost of AWE plant;
- Electrolyser Stack Replacement cost for the AWE plant;
- Variable non-electrical costs for the AWE plant;
- O&M costs for the AWE plant.

In the following sections, the data used for the economic analysis will be introduced, and the models created to evaluate the investments will be explained, firstly for the Water Electrolysis Plant, and then for the High Temperature Steam Electrolysis and the Sulfur-Iodine ones.

The MC analysis has been performed only for the WEP. The investment on the other plants have been studied just with a Deterministic approach.

4.2 Alkaline Water Electrolysis

4.2.1 Model steps

Since for a given production capacity there are fixed costs (that are sunk), and the revenue and variable costs generally increase linearly (which means that marginal revenues and marginal costs are constants), the aim of a plant is normally to achieve its nominal production.

This is not the case of a WEP, because the marginal cost is not a constant, but it increases: indeed this last is constituted by the electrical cost [69], which depends on the electricity price.

Several studies assert that AWE is not economically competitive because of the high cost of electricity [37], [79]. But in these cases, the 24 hours operation, or a combination with must-run power sources (like wind or PV) [138], [144] have been assessed.

The present study shows how, since the main cost is represented by electricity, the profitability of the investment depends also on the number of operating hours.

4.2.1.1 Step 1: Deterministic DCF

The DCF model is composed as in the following following Table 4-1:

Year	**0**	**1**	**2**	**…**	**40**
Capital Cost [M€]	C_C	0	0	…	0
O&M costs [M€]	0	O_C	O_C	…	O_C
Electrical Costs	0	E_C	E_C	…	E_C
Other NE costs	0	NE_c	NE_c	…	NE_c
Stack Replacement Cost [M€]	0	SR_C	SR_C	…	SR_C
Hydrogen Revenues [M€]	0	H_R	H_R	…	H_R
Reserve	0	R_{UP}	R_{UP}	…	R_{UP}

utilisation payment[M€]					
Reserve availability payment [M€]	0	R_{AP}	R_{AP}	…	R_{AP}
Net [M€]	$-C_c$	Net $=(H_R+R_{UP}+R_{AP})-(O_C+E_C+NE_c+SR_C)$	…	…	…
Cumulative Cash Flow [M€]	$-C_c$	$\sum_{i=0}^{1}\frac{Net}{(1+WACC)^i}$	…	…	$\sum_{i=0}^{40}\frac{Net}{(1+WACC)^i}$

Table 4-1: WEP DCF calculation scheme

As for the cost items, have been considered:

- Capital Cost, which basically consists in the purchase and deployment of the stacks (that are delivered as pre-assembled units). This requires a relatively brief time (from weeks to some months, according to the manufacturers) so the construction of the WEP is assumed to be started and completed at the year 0, and the operation starts at year 1;
- Operation & Maintenance Costs;
- Electrical Costs, due to the purchase of electricity at the market price. Since in any operation mode there are two operational periods (day and night), each of which has a typical average EP, the electricity costs are separated into two elements: Day Electricity' and 'Night Electricity';
- Other Non-Electrical Costs, which consider other (almost negligible) cost items (as demineralised feedwater consumption) are assumed as 1% of the total annual costs;
- Stack Replacement costs: as already explained, while the estimated life for the WEP is 40 ([63] 16., 18.) years, the stacks (i.e. the part of the EZ where the electrochemical reactions take place) suffer degradation problems, so they need to be replaced every 9-10 years ([63] 16., 18.). This value is the expected one for one EZ, but it is not realistic that all the 304 EZs have exactly the same lifetime. Since the number of EZs is so large, an average functioning is forecast, and an annual cost of Stack Replacement is considered: the total cost of one Stack Replacement is divided by 10, and spread over the 10 years of lifetime.

There are three different items of revenues:

- from the selling of Hydrogen (for easiness, the revenues coming from the 'Day Operation' and 'Night Operation' are kept separated);
- from the *EE actually sold* as 'Reserve' (STOR or FR, depending on the considered case);
- from the payment for the *availability hours*, in the operation cases involving the Reserves (STOR or FR, again).

In Table 4-2 are described the Cost and Revenues items during the different periods of the Base Case 8 operation mode.

Operation description	**Cost items**	**Revenues items**	**Hours**
Day operation: (304 EZs at 20%)	• EE bought: 134 MW	• H_2 production (from 134 MW)	5,840
Night operation	• EE bought: 669 MW	• H_2 production (from 669 MW)	2,920

Table 4-2: Cost and Revenues description during different operation periods in BC 8

For the BC 12 case, the principle is the same, just with a different number of hours.

The cases of Reserve operation require a deeper analysis regarding the associated costs and revenues (see section 4.2.1.4).

The Deterministic DCF model, even when computed considering three scenarios (most likely, optimistic and pessimistic, obtained inputting the extreme values of technical and economic inputs), presents two insuperable limits:

- the Mean value of Electricity Price, which is the essential factor in the WEP cost analysis, can change even markedly year by year, as can be seen from the 2013 and 2014 values [36];
- the Hydrogen Price, which determines the Revenues is very difficult to estimate, and more difficult to forecast even in the near future, because of different factors:
    - the most part of the Hydrogen production worldwide is finalized to self-consumption, and just a few percent of it is actually traded [29];
    - because of this reason, the scientific literature present several works dealing with hydrogen production cost, but not with its selling price;
    - different companies which trade technical gases and hydrogen in particular have been contacted in order to figure out a possible hydrogen selling price, but no one has been capable to answer this question. The pressure and purity, and the exact geographic area where the hypothetical WEP is placed (to assess the possible buyers) would be necessary to perform this kind of evaluation, that would be in any case subjected to great uncertainties.

Considering this, the Det DCF loses most of its capability to access the profitability of the investment, because it specifically focuses on a specific scenario (in particular in terms of hydrogen price).

To overcome these limits a different approach is adopted, in the following part of this research study.

4.2.1.2 Step 2: Deterministic breakeven H_2 price

The aim of this step is to calculate the *deterministic breakeven H_2 price*, i.e. the price for which NPV over 40 years life cycle of the plant is equal to zero, which means that invest or not to invest are options bringing exactly to the same output.
This is a very powerful tool for this analysis, as it allows to answer to the following question: *starting from a certain electricity price scenario, what is the minimum price that the hydrogen should have for the Load Following by off-peak hydrogen production (via AWE) to be a profitable investment?*

This let the reader to consider the presented results very general either from a geo*graphical and temporal standpoint*, so that they allow to reach conclusions for the UK market, but can be applied to other countries, characterized by different Mean values of the EPD.

Three scenarios are investigated: expected case (where the expected value of each data set is inserted in the model), best case (minimum values of each cost item, and maximum of plant performance), and worst case (the contrary, with respect the best case).

However even this description does not narrowly describe the risk associated with the investment, when, like in this study, the best/worst case probability to occur is actually 0. This because the uncertain parameters occur according to a probability distribution, which tends to 0 at the extremes. When several distribution are combined, the output is again a distribution, whose extreme values have a very little probability to occur. For instance, in order the best case to happen *every* parameter should assume its *optimistic* value.
Thus, a Montecarlo analysis is performed.

From the practical point of view, once the DCF model is designed, this step is implemented using the Excel function *goalseek* on the NPV cell, letting the algorithm changing the hydrogen price cell.

4.2.1.3 Step 3: Montecarlo analysis

The next step represents in principle the same concept of step 3, but this time the input cells (technical and economic) are MC distributions (see section 4.2.2). In this case the algorithm is supported by @Risk, through the function *riskgoalseek*.

Thus finally, for each electricity price scenario, three breakeven hydrogen prices are obtained:

- the Mean value of the breakeven hydrogen price distribution;
- the 5 percentile of the breakeven hydrogen price distribution, which means that there is only a 5% of probability that the *real* breakeven hydrogen price is superior than this value (that is a pessimistic case);

- the 95 percentile of the breakeven hydrogen price distribution, which means that there is a 95% of probability that the *real* breakeven hydrogen price is superior than this value (that is an optimistic case).

4.2.1.4 Step 4: Assessment of Electricity Reserves: STOR and FR

Once all the steps are made for the Base Cases, the possibility of a further profitability consisting in operating the EZs as Electricity Reserves is evaluated.

The production, and so the costs and revenues coming from these operation modes are computed in the same way as for the Base Cases.

In Table 4-3 and Table 4-4 is presented a description of the sustained costs and revenues for the STOR and the FR operating modes. Only the costs and revenues which distinguish these cases from the Base Case 8 are specified here.

Operation description	**Cost items**	**Revenues items**	**Hours**
Day operation: (279 EZs at 20%)	- EE bought: 122 MW	- H_2 production (from 122 MW)	5,840
Availability – ready state (25 EZs at 100%)	- EE bought: 55 MW	- H_2 production (from 55 MW) - Availability payment	3,864
Selling Electricity (STOR)	- Not produced H_2 (from 55MW)	- Utilisation payment: EE sold on STOR market	78

Table 4-3: Cost and Revenues description during different operation periods in STOR

Operation description	**Cost items**	**Revenues items**	**Hours**
Day operation: (259 EZs at 20%)	- EE bought: 114 MW	- H_2 production (from 114 MW)	5,840
Availability – ready state (45 EZs at 100%)	- EE bought: 99 MW	- H_2 production (from 99 MW) - Availability payment	4,223
Selling Electricity (STOR)	- Not produced H_2 (from 99MW)	- Utilisation payment: EE sold on FR market	365

Table 4-4: Cost and Revenues description during different operation periods in Fast Reserve

4.2.2 Data for the analysis

In this section all data inserted in the model in matter of costs are reported. A comparison between costs reported in literature has already been done, so here can be found only the data which actually represent an input for the model. Costs needed to be introduced regard only the hydrogen plant, but not the nuclear reactor. Indeed we specify again that we assume that the construction of the nuclear site is already planned and confirmed. With this work we want to investigate only if it is possible to enlarge the investment's worth, taking advantage of the wasted energy. Therefore the suitability of the investment in the nuclear reactors is not discussed and consequently overnight costs and operation and maintenance costs (O&M) for the NPPs are not considered.

Technical data have been already listed in section 3.2; here the economic data are presented.

As for the CAPEX, the manufacturers have been questioned in detail. They normally deliver all modules required for the full production of the hydrogen at the given capacity, pressure and purity. In the 'standard delivery' are included: Transformer, Rectifier, Electrolyser, Electrolyte system (including gas separators), Gas Scrubber, Gas Holder, Gas Analysers, Control Panel. Moreover, if required, they also delivery, with an additional cost, the Water Purification Unit, Dryer, Deoxidiser, and Compressor.
They underline that it is not simple to forecast the cost of the complete equipment, especially for a large scale requirement, since the sizing of capacity for both compressors and dryers/deoxidisers needs to be carefully analysed and agreed to. I.e. it might be one compressor and dryer/deoxidiser for every 4 or 5 electrolyser, and that would have a great influence on the total capex. Additionally, for the compressors, the required outlet pressure may vary largely, and will also have a big influence on the capex. This may need to be analysed also with the storage requirement and costs. They may also deliver gas storage vessels, but as this often may be sourced from a local producer, they do it rarely .
Under this premise, the manufacturer estimates a 650 €/kW CAPEX for the basic equipment, and:

- For dryer/deoxidizer in large scale solution, it is estimated an increaseof the capex of 3-6%.
- For the ompressor the variation could be larger, depending on configuration and pressure. An addition of 10-30% is estimated.

This leads to the CAPEX expected and extremes values that can be found in Table 4-5.

As for the OPEX and Stack Replacement, the expected values are taken both according to the literature [71] and the estimates of manufacturers. The extreme values are taken according to the uncertainties combines to the costs usually used in literature in matter of economic analysis [12].

		Expected value	Min	Max	IS unit
COSTS	**CAPEX**	0.81	0.73	0.88	k€/kWe
	OPEX [% capex]	1.25%	1.0%	1.5%	-
	Variable non electrical cost [% total costs]	1.0%	0.9%	1.1%	-
	Stack Replacement [% capex]	50%	45%	55%	-
PRICES	**Hydrogen price**	0.40 until step 1; then research goal	/	/	€/Nm3_H2
	Electricity price	Scenario variable: {0.02; 0.04; 0.06; 0.08; 0.10}			€/kWh
	Discount rate	5%	/	/	-

Table 4-5: WEP Economic Inputs

The considered expected values are taken according to the literature, as explaned in section 2.4; then the distributions for the values are always defined as Pert function, since this latter is the most common distribution used in literature.

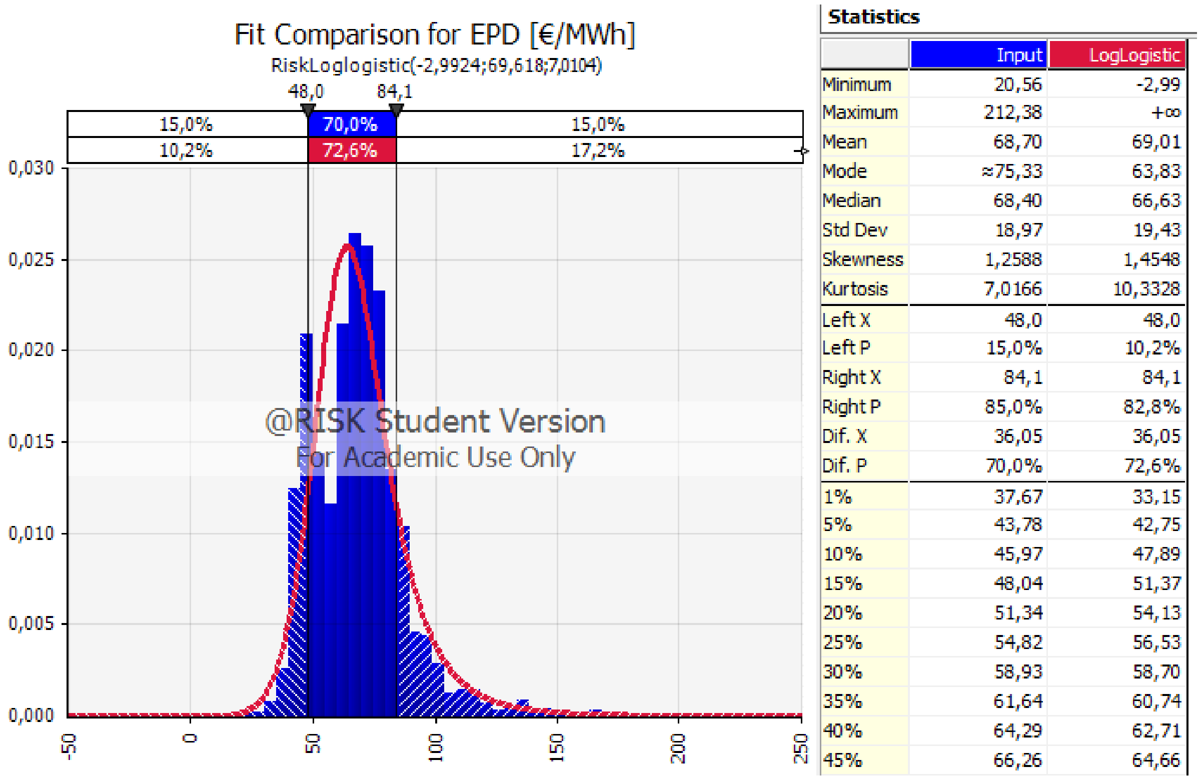
Distributions are inserted within the sheets and are simulated with Monte Carlo method, thanks to @Risk tool (of Palisade Decision Tool) for Microsoft Excel.
Regarding costs, the values inserted in the balance sheet are simply extracted from the distributions. For example, if the nominal value of OPEX for the AWE plant is assumed to be 1.25 % of the CAPEX, the range that characterizes this distribution will be between 1.35 and 1.65 %.

In Table 4-6 the extreme values of the Pert distributions are listed.

ITEM	DISTRIBUTION TYPE	EXTREME VALUES
CAPEX	Pert Distribution	{0.73;0.81;0.88}
OPEX	Pert Distribution	{1.0%; 1.25%; 1.5%}
Variable non electrical cost	Pert Distribution	{0.9%;1.0%;1.1%}
Stack Replacement	Pert Distribution	{45%; 50%; 55%}

Table 4-6: Extreme values of the Pert Distribution for each Cost Item

Regarding the electricity price, different prices for the night and day electricity are used in the simulations.
The hourly EP is variable during the year: the EP distribution of UK Day Ahead electric market of year 2013 is available online [36].



Statistics

	Input	LogLogistic
Minimum	20,56	-2,99
Maximum	212,38	+∞
Mean	68,70	69,01
Mode	≈75,33	63,83
Median	68,40	66,63
Std Dev	18,97	19,43
Skewness	1,2588	1,4548
Kurtosis	7,0166	10,3328
Left X	48,0	48,0
Left P	15,0%	10,2%
Right X	84,1	84,1
Right P	85,0%	82,8%
Dif. X	36,05	36,05
Dif. P	70,0%	72,6%
1%	37,67	33,15
5%	43,78	42,75
10%	45,97	47,89
15%	48,04	51,37
20%	51,34	54,13
25%	54,82	56,53
30%	58,93	58,70
35%	61,64	60,74
40%	64,29	62,71
45%	66,26	64,66

Figure 4-1: UK 2013 hourly EPD [€/MWh], BLUE: real values; RED: LogLogistic, best fitting distribution

In the Table 4-7 are presented the values, extracted from the 2013 and 2014 EPDs [36]. Figure 4-1 shows the fitting of the UK 2013 hourly electricity price distribution. The distribution which best fits the Real EPD is the LogLogistic (defined by three parameters: {α;β;γ} = {-2.9924; 69.618; 7.0104}, as is visible in Figure 4-1) .

	Real EPDs [€/kWh]					
	Mean [€/kWh]	Standard Deviation	Average 33%ile	Average 50%ile	Average 66%ile RIGHT	Average 50%ile RIGHT
2013	0.069	0.019	0.050	0.055	0.078	0.083
2014	0.058	0.016	0.061	0.047	0.064	0.068

Table 4-7: Real Electricity Price Distributions, key values

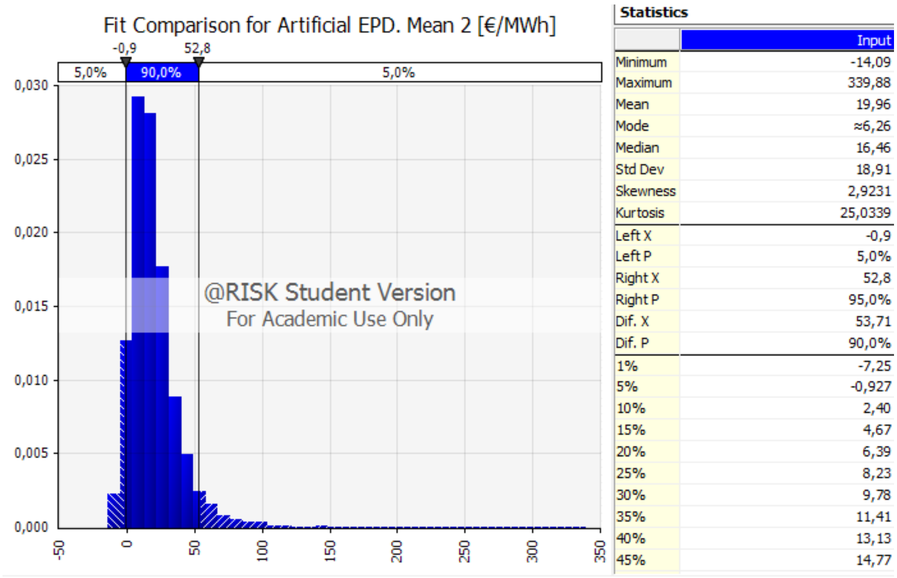
The values listed in the table have the following meaning:

- First column: the mean value. As can be seen there is a difference of 11 c€/kWh (almost 16%) between the two years, which proves how electricity price can vary greatly even in the same market, within a brief period of time;
- Second column: the standard deviation of the distribution, which mostly determines the shape (wide or narrow) and is crucial for the Load Following. In 2014 the EPD was more narrow, so there has been less margin to take advantage on the spread between the day and night EP.
- Third column: it is the average value of the less expensive 2,920 hours of the year (1/3 of the hours = 8 hours/day). Assuming that these follow mainly

during the night, this is the average EP that is used for ‘Night Operation’, in the assessment of the BC 8 operating mode.

- Fourth column: : it is the average value of the less expensive 4380 hours of the year (1/2 of the hours = 12 hours/day). This is the average EP that is used for the ‘Night Operation’, in the assessment of the BC 12 operating mode.
- Fifth column: it is the average value of the most expensive 5840 hours of the year (2/3 of the hours = 16 hours/day). This is the average EP that is used for ‘Day Operation’, in the assessment of the BC 8 operating mode.
- Sixth column: it is the average value of the most expensive 4380 hours of the year (1/2 of the hours = 12 hours/day). This is the average EP that is used for the ‘Day Operation’, in the assessment of the BC 12 operating mode.

In order to make the model as general as possible, several different scenarios have been considered for the simulations: varying from very cheap to very expensive electricity. Varying the input parameters of the LogLogistic distribution, artificial EPDs have been created, maintaining approximately the same Standard Deviation of the Real EPD, but changing the Mean value. For instance, the fitting of the EPD with Mean 20 €/MWh is shown in Figure 4-2.



Statistics

	Input
Minimum	-14,09
Maximum	339,88
Mean	19,96
Mode	≈6,26
Median	16,46
Std Dev	18,91
Skewness	2,9231
Kurtosis	25,0339
Left X	-0,9
Left P	5,0%
Right X	52,8
Right P	95,0%
Dif. X	53,71
Dif. P	90,0%
1%	-7,25
5%	-0,927
10%	2,40
15%	4,67
20%	6,39
25%	8,23
30%	9,78
35%	11,41
40%	13,13
45%	14,77

Figure 4-2: Artificial EPD. Mean 20 [€/MWh]

All the values extracted from the artificial EPDs used in the simulations (also for the HTSE and SI Plants investigations), are listed in Table 4-8

Artificial (LogLogistic) EPDs [€/kWh]					
Mean [€/kWh]	St Dev	aver 33%ile	aver 50%ile	aver 66%ile DX	aver 50%ile DX
0,02	19	0,041	0,074	0,28	0,33
0,04	19	0,23	0,27	0,49	0,54
0,06	19	0,42	0,46	0,69	0,74
0,08	19	0,62	0,66	0,89	0,94
0,10	19	0,81	0,86	1,09	1,14

Table 4-8: Artificial EPDs characterization

The hydrogen price is very complex to define, since as already explained, the most part of the produced hydrogen is not traded, but consumed 'in situ' [29]. According to the technical gas companies that have been contacted ([63], 22.), the price at which they would buy the produced hydrogen (which anyway would represent a huge production) depends on several parameters, which include geographical factors (the state and the specific region where the AWE plant operates), the presence in a medium-short range of chemical plants that require hydrogen, or (in the future) of systems of distribution of hydrogen for the private mobility, and so on.

In other words, the price of 0.40 €/Nm^3, indicated as approximate value by an EZ manufacturer ([63], 18.), is simply indicative and could reveal very optimistic in certain contexts.

This is the reason why this value has been used just until the step 3 of the model, and then the hydrogen breakeven price of the investment is investigated, as output of the research study.

The payment data and the derived revenues (with original data converted in €) for STOR and FR are presented in Table 4-9 and Table 4-10, respectively:

STATUS: Short Term Operating Reserve	**Availability (contracted)**	**Utilisation**	**Not Contracted**
Hours per year	3,864	78	4,818
Unitary payment [€/MWh]	3.36	212	0
Total year revenue for 55 MWe [k€]	648	827	0

Table 4-9: Short Term Operating Reserves - Revenue calculation (data converted in €)

STATUS: Fast Reserve	**Availability (contracted)**	**Utilisation**	**Not Contracted**
Hours per year	4,223	365	4,912
Unitary payment For a 99 MW Reserve plant	814 [€/h]	192 [€/MWh]	0
Total year revenue for 99 MWe [k€]	3,551	7,000	0

Table 4-10: Fast Reserve - Maximum Revenue calculation (data converted in €)

It can be seen how compressively the STOR operation (not taking into account neither hydrogen revenues nor other costs) provides a further revenue of approximately 1.4 M€/year, while the FR even causing a certain damage to the EZs, can provide up to 10.2 M€/year of extra revenue. This makes the FR particularly attractive.

Finally, the Discount Rate (WACC) is taken equal to 5%, which is a standard value for economic analysis which does not consider the inflation.

4.3 HTSE

4.3.1 Model

4.3.1.1 HTSE Deterministic DCF

Starting from the technical results, a DCF model (Table 4-11) is presented in this section. The only relevant differences from the WEP DCF model are:

- The presence of the Electrical & *Thermal* costs. This cost item corresponds to the missing revenue (from the NPP standpoint) due to the not sold electricity, so the amount paid by the HTSE owner to buy the energy. The Day not sold electricity is multiplied by the average Day EP (average of the 16 more expensive hours of the day), and the same is made for the night by the Night EP;
- The Natural Gas fuel cost, which is present only in the PWR+NG case;
- The absence of Reserves revenues, since the effect of the Reserves is not assessed for the HTSE Plant;

The observations made on the uncertainties of the Electricity Price and the possible Hydrogen selling price in section 4.2.1 are still valid, so different scenarios regarding their values are considered here.

Year	0	1	2	…	20
Capital Cost [M€]	C_C	0	0	…	0
O&M costs [M€]	0	O_C	O_C	…	O_C
Electrical & Thermal Costs	0	E_C	E_C	…	E_C
Other NE costs	0	NE_c	NE_c	…	NE_c
Stack Replacement Cost [M€]	0	SR_C	SR_C	…	SR_C
Natural Gas costs [M€]	0	NG_C	NG_C	…	NG_C
Hydrogen Revenues [M€]	0	H_R	H_R	…	H_R
Net [M€]	$-C_c$	Net $=H_R-(O_C+E_C+NE_c+SR_C+NG_C)$	…	…	…
Cumulative Cash Flow [M€]	$-C_c$	$\sum_{i=0}^{1}\frac{Net}{(1+WACC)^i}$	…	…	$\sum_{i=0}^{20}\frac{Net}{(1+WACC)^i}$

Table 4-11: HTSE Plant DCF model

4.3.1.2 SOEC breakeven capex

Since the technology is not ready to be commercialized it is really difficult to forecast a credible CAPEX for the SOEC model, despite some attempts discussed in **Errore. L'origine riferimento non è stata trovata.**. Thus, for this technology (and the same is for the SI cycle, section 4.4), the most interesting research output is the *breakeven CAPEX*.

This is the maximum cost for a SOEC module which would imply (in a certain scenario made by an Electricity Price, an Hydrogen Price, and a level achieved by technology development, represented by a certain efficiency degradation) an investment with an NPV equal to zero. It is obvious that if the technology achieve a CAPEX which is minor than the one obtained by model, in the same scenario, then the investment would be profitable, otherwise it would be not.

4.3.2 Data

The economic inputs for the HTSE DCF are listed in Table 4-12:

		Value	IS unit
COSTS	**CAPEX**	Research goal	k€/(kilo Nm^3/h)
	OPEX [% capex]	1.5%	-
	Variable non electrical cost [% total costs]	1%	-
	Stack Replacement [% capex]	50%	-
PRICES	**Hydrogen price**	Scenario variable: {0.15; 0.30; 0.45}	€/Nm3_H2
	Electricity price	Scenario variable: {0.02; 0.04; 0.06; 0.08; 0.10}	€/kWh
	Natural Gas price	0.0091	€/kWh_th
	Discount rate	5%	-

Table 4-12: HTSE Deterministic DCF Inputs

In particular:

- The CAPEX is the research goal of this analysis, thus it is the object of a goal seek;
- While in literature they are considered together [105], in this study the OPEX and Stack Replacement are treated separately. This because the level that the technology will achieve cannot be predicted, so this is taken into account by considering different efficiency degradation rates (see section 3.4.2), which directly influences the number of replacements that are needed in 10 years, and in turn the Stack Replacement Costs. Thus, they are assumed the same of the Water Electrolysis Plant, in terms of % of CAPEX;
- The prices of hydrogen and electricity are Scenario variables;
- The natural gas price is taken equal to 0.91 c€/kWh_th [88].

4.4 SI cycle

4.4.1 Model

Starting from the technical results, a DCF model (Table 4-13) is presented in this section.
The only relevant differences from the HTSE DCF model are:

- The presence of only *Thermal* costs, computed as the cost of the Not Sold Electricity;
- The absence of the Stack Replacement Cost, because of the different (not modular) nature of the plant;
- The absence of Natural Gas fuel cost, because the PWR+NG case is not studied, due to its evident unfeasibility (see section 3.5);

The observations made on the uncertainties of the Electricity Price and the possible Hydrogen selling price in section 4.2.1 are still valid, so different scenarios regarding their values are considered here.

Year	**0**	**1**	**2**	**…**	**20**
Capital Cost [M€]	C_C	0	0	…	0
O&M costs [M€]	0	O_C	O_C	…	O_C
Thermal Costs	0	E_C	E_C	…	E_C
Other NE costs	0	NE_c	NE_c	…	NE_c
Hydrogen Revenues [M€]	0	H_R	H_R	…	H_R
Net [M€]	$-C_c$	$Net = H_R - (O_C + E_C + NE_c)$	…	…	…
Cumulative Cash Flow [M€]	$-C_c$	$\sum_{i=0}^{1} \frac{Net}{(1+WACC)^i}$	…	…	$\sum_{i=0}^{20} \frac{Net}{(1+WACC)^i}$

Table 4-13: SI cycle Plant DCF model

4.4.2 Data

The economic inputs for the SI cycle DCF are listed in Table 4-14:

		Value	IS unit
COSTS	**CAPEX**	Research goal	k€/(kilo Nm^3/h)
	OPEX [% capex]	Scenario variable: {2.5%; 5%; 7.5%; 10%}	-
	Variable non electrical cost [% capex]	1%	-
PRICES	**Hydrogen price**	Scenario variable: {0.15; 0.30; 0.45}	€/Nm3_H2
	Electricity price	Scenario variable: {0.02; 0.04; 0.06; 0.08; 0.10}	€/kWh
	Discount rate	5%	-

Table 4-14: SI cycle Deterministic DCF Inputs

- The CAPEX is the research goal of this analysis, thus it is the object of a goal seek;
- In this case there are no stacks and no modules. Costs. Thus, they are assumed the same of the Water Electrolysis Plant, in terms of % of CAPEX;
- The prices of hydrogen and electricity are scenario variables.

5 Results

In this chapter, the final results of the economic analysis performed for each technology are reported. Firstly the results are presented and explained, then in the last section of each paragraph, a discussion on the results is made.

5.1 AWE

5.1.1 Deterministic DCF

In this section is presented the calculation of the Deterministic NPV of the investment in the WEP.

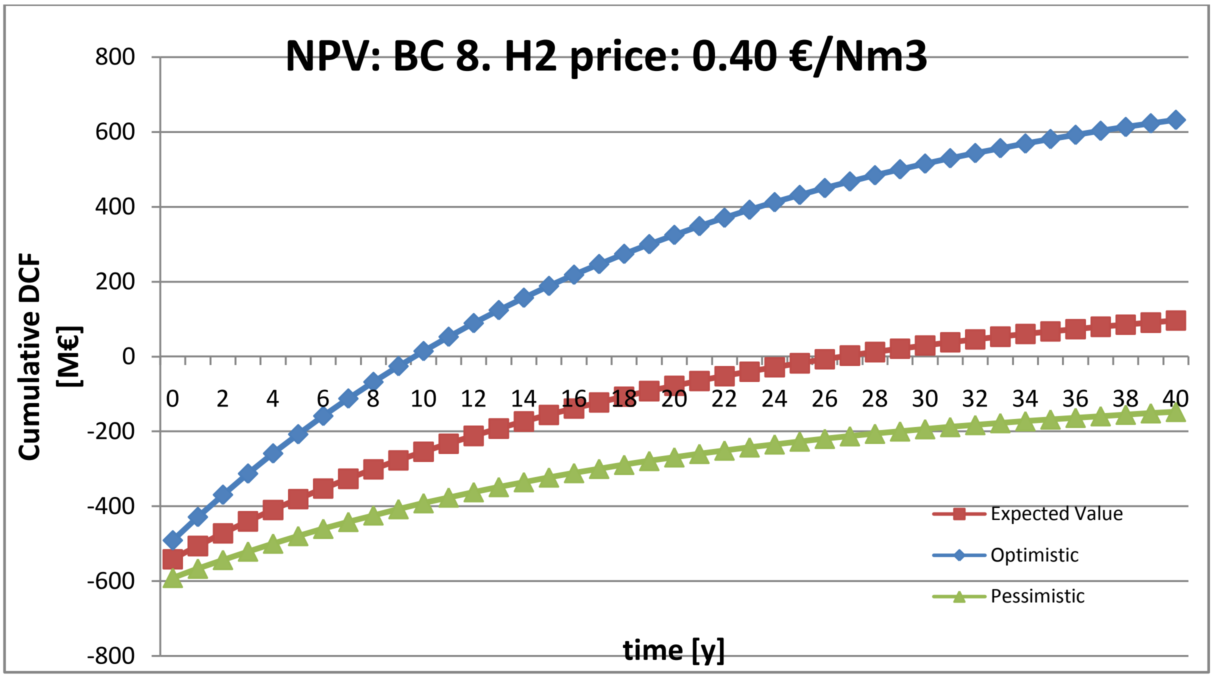


Figure 5-1: Net Present Value for the Base Case 8 operation, taking the Hydrogen price at 0.40 €/Nm3.

The graphic in **Errore. L'origine riferimento non è stata trovata.** shows the variation of the Cumulative Discounted Cash Flow over the whole life of the WEP (40 years). An Hydrogen price of 0.40 €/Nm^3 is hypothesized. It is calculated for a Base Case 8 operation, and three scenarios (Expected value, Optimistic and Pessimistic) are considered. The value of the Cumulative DCF in the last year is the Net Present Value of the investment. The three scenarios present very different results: indeed, it can be seen that in the best case the Pay Back Time is about 9 years, in the Expected scenario is 25 years, while the pessimistic one forecast a not profitable investment. Moreover, Figure 5-2 shows that the uncertainties on technical and cost inputs (that constitute the difference between the Optimistic and Pessimistic scenarios) are not the variable having the main impact on the investment: the hydrogen price it is. Indeed, in Figure 5-2 is shown the cumulative DCF for the BC 8 operation, with an Hydrogen price of 0.30 €/Nm^3: the results change widely. In particular, with an hydrogen price of 0.30 €/Nm^3, the NPV is negative for all the scenarios.

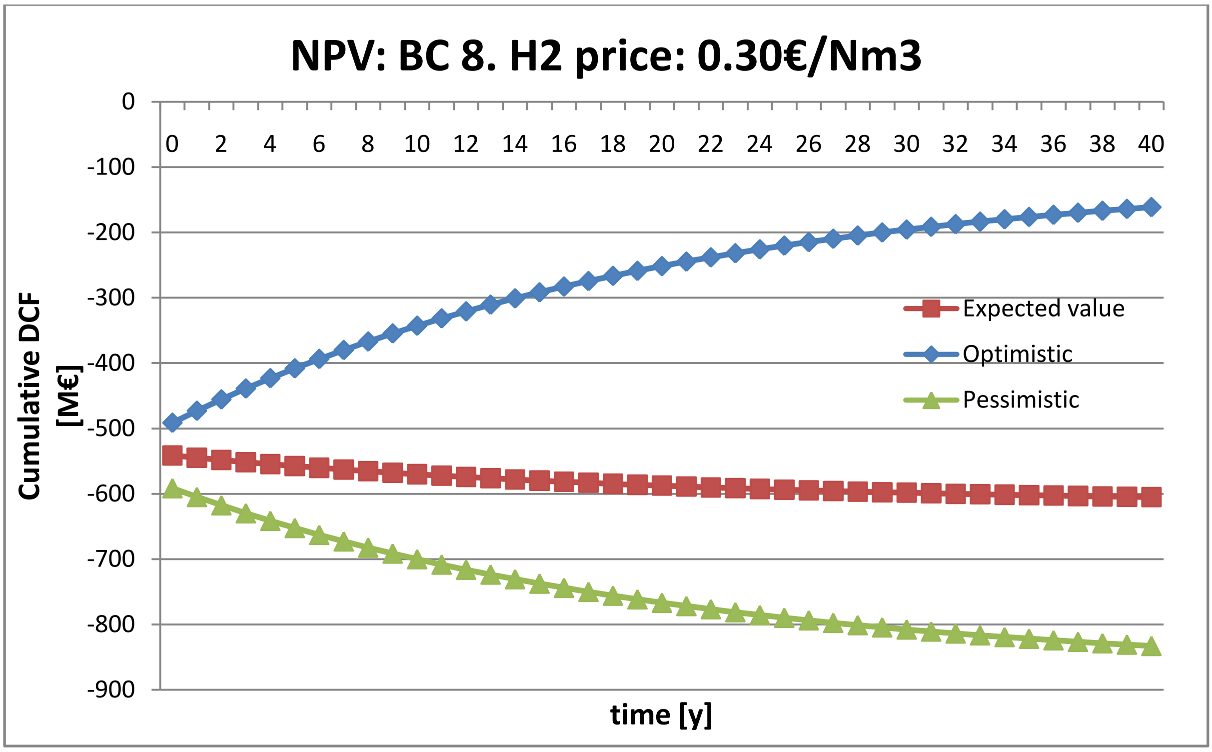


Figure 5-2: Net Present Value for the Base Case 8 operation, taking the Hydrogen price at 0.30 €/Nm3.

This results explain why it is essential to perform the economic analysis by the hydrogen breakeven price approach.

5.1.2 Deterministic hydrogen breakeven price

In this section is presented the calculation of the hydrogen breakeven prices, according to the two Base Case scenarios: BC 8 and BC 12.

Deterministic BC 8			
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Expected value	Optimistic	Pessimistic
0,02	0,18	0,14	0,21
0,04	0,26	0,21	0,30
0,06	0,35	0,29	0,39
0,08	0,44	0,37	0,48
0,1	0,53	0,44	0,57

Table 5-1: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Base Case 8 operation mode

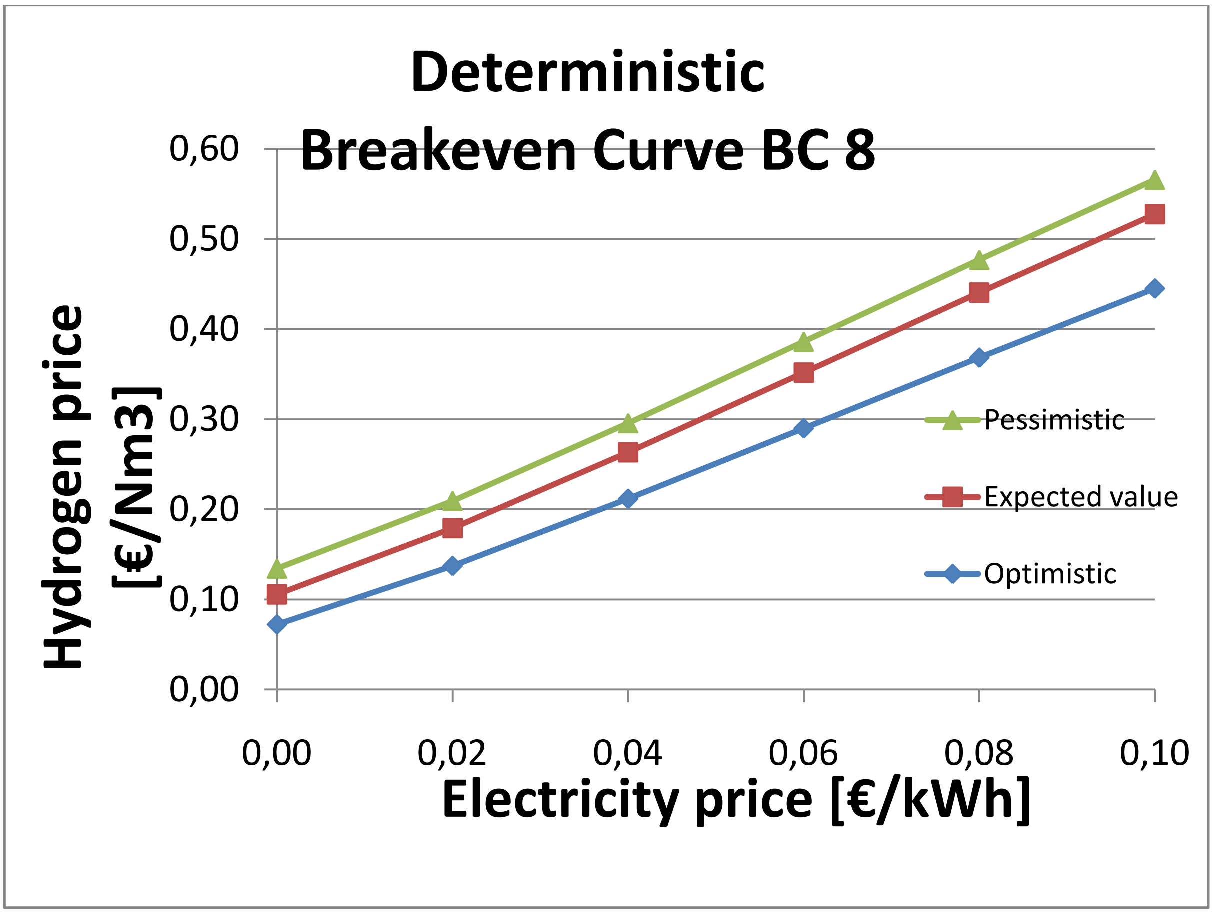


Figure 5-3: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic curves. Base Case 8 operation mode

Then, the Base Case 12 table and graphic, which presents the same shape of the Figure 5-3, just with different values.

Deterministic BC 12			
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Expected value	Optimistic	Pessimistic
0,02	0,14	0,11	0,16
0,04	0,23	0,19	0,25
0,06	0,32	0,27	0,34
0,08	0,41	0,35	0,43
0,1	0,49	0,42	0,52

Table 5-2: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Base Case 12 operation mode

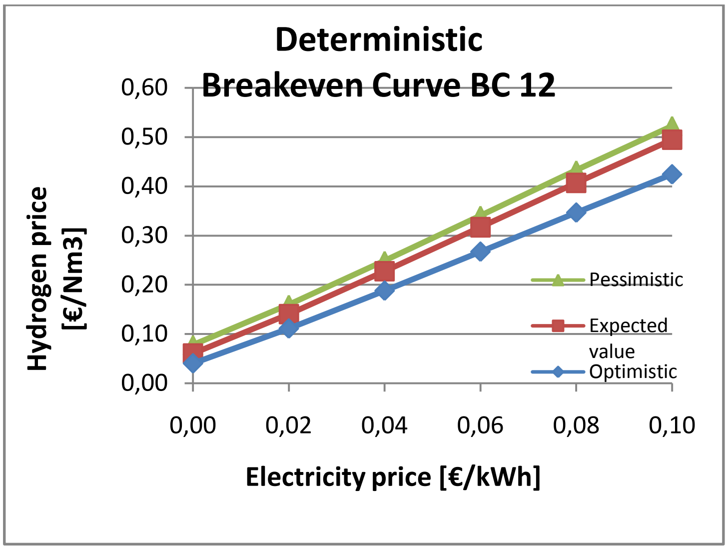


Figure 5-4: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic curves. Base Case 12 operation mode

This model is very flexible and has the aim to be as much as general possible. In particular, the aim is not to study the applicability of a cogenerative plant in a selected country. The goal of this work is to study the eventual profitability of such a plant, in the real uncertain market. Therefore, defined scenarios are not limited to precise and very specific parameters. They want to provide some outputs, in relation to the variations of some peculiar inputs. Thus, starting from a country characterized by a certain Electricity Price Distribution with a certain Mean, in these graphics can be found the minimum price at which the produced hydrogen should be sold in order to have a profitable investment. If the hydrogen price is above this value, the WEP can be planted and made operate; otherwise not.

5.1.3 Montecarlo analysis

In this section the results of the Montecarlo simulations on the BC 8 and BC 12 cases are presented.

Montecarlo BC 8			
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Mean MC	95%ile MC	5%ile MC
0,02	0,18	0,16	0,19
0,04	0,25	0,23	0,27
0,06	0,35	0,33	0,36
0,08	0,43	0,41	0,45
0,1	0,52	0,49	0,54

Table 5-3: Montecarlo Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Base Case 8 operation mode

In the three column the scenarios considered by the MC simulation are listed. The Mean MC represents the Mean value of the Breakeven Hydrogen price distribution. The 95 Percentile and 5 Percentile take the place of Optimistic and Pessimistic scenarios, respectively. But, as can be seen in Figure 5-5, which represents the curves both from the Deterministic and Montecarlo analysis, these two curves are much closer to the Mean one (which almost coincides with the Expected value). Thus, as reasonably expected, while paying a significantly heavier computational cost, the MC simulation narrows the margin of uncertainty on the hydrogen breakeven price.

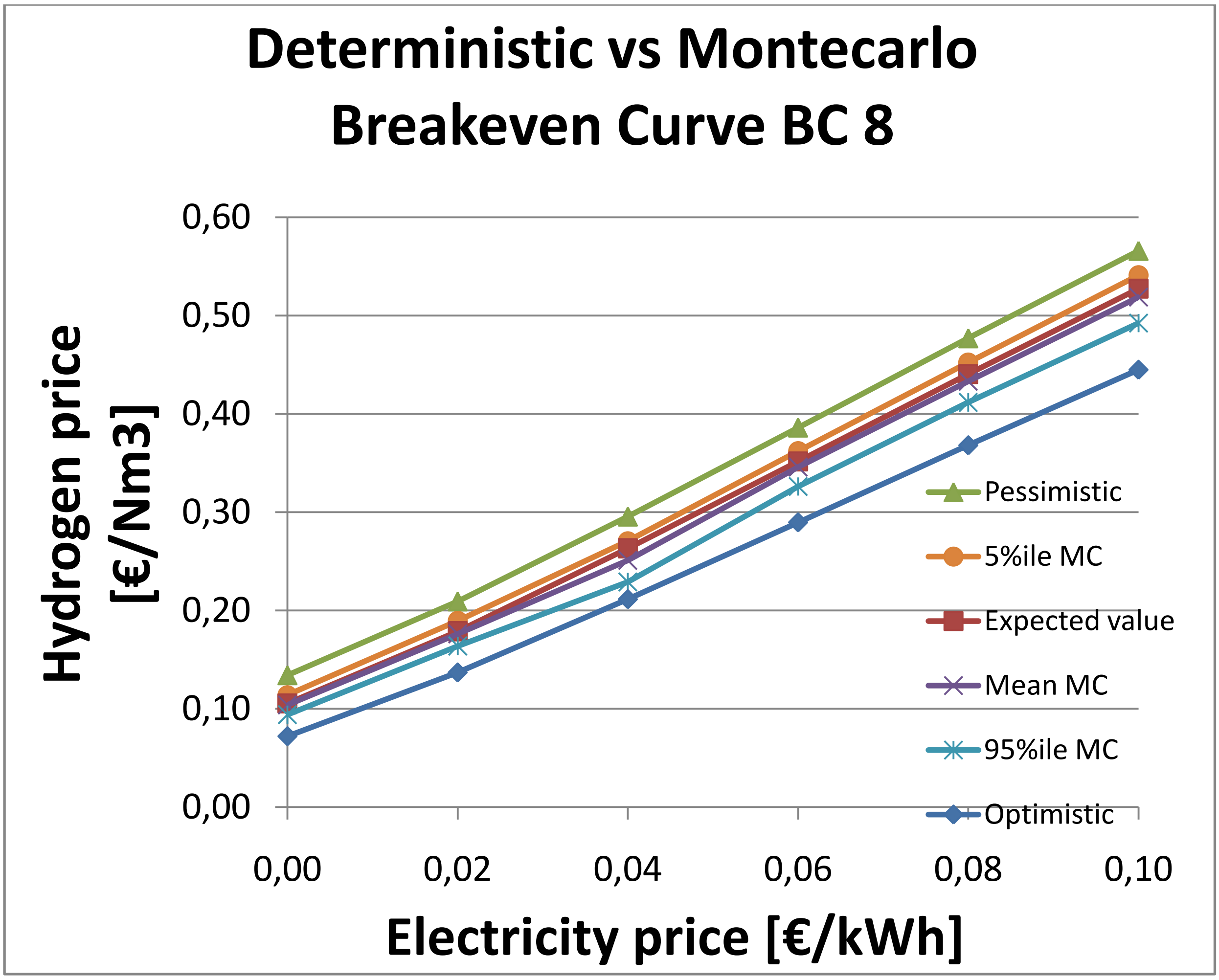


Figure 5-5: Deterministic and Montecarlo Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic, Pessimistic, Mean, 5 Percentile and 95 Percentile curves. Base Case 8 operation mode

The same considerations are valid for the MC simulation results on BC 12 operation , which are presented below.

BC 12			
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Mean MC	95%ile MC	5%ile MC
0,02	0,14	0,13	0,15
0,04	0,22	0,21	0,23
0,06	0,31	0,30	0,32
0,08	0,40	0,38	0,41
0,1	0,49	0,47	0,50

Table 5-4: Montecarlo Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Base Case 8 operation mode

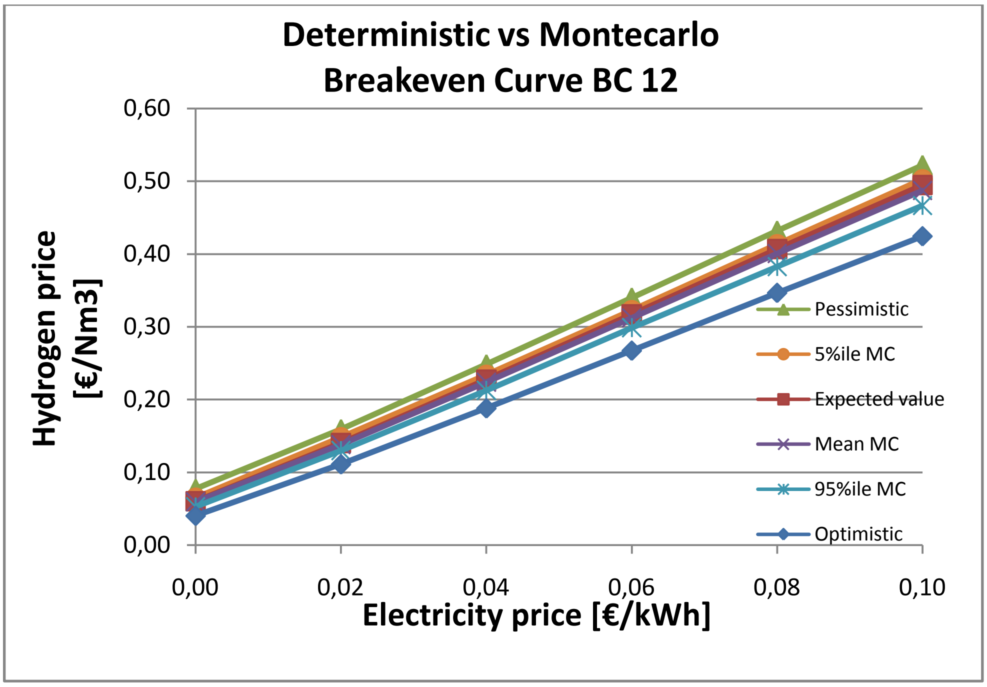


Figure 5-6: Deterministic and Montecarlo Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic, Pessimistic, Mean, 5 Percentile and 95 Percentile curves. Base Case 12 operation mode

5.1.4 Assessment of Electricity Reserves

In this section is presented the calculation of the hydrogen breakeven prices, according to the Reserve scenario: STOR, FR 2, FR 5, FR 10, FR 20.

STOR			
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Expected value	Optimistic	Pessimistic
0,02	0,16	0,13	0,19
0,04	0,25	0,20	0,28
0,06	0,34	0,28	0,37
0,08	0,43	0,36	0,46
0,1	0,51	0,44	0,55

Tabele 5-5: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. STOR operation mode

FR degradation factor			2
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Expected value	Optimistic	Pessimistic
0,02	0,15	0,12	0,17
0,04	0,24	0,20	0,26
0,06	0,33	0,28	0,35
0,08	0,42	0,36	0,44
0,1	0,51	0,43	0,54

Table 5-6: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Fast Reserve (degradation factor = 2) operation mode

FR degradation factor			5
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Expected value	Optimistic	Pessimistic
0,02	0,16	0,12	0,18
0,04	0,24	0,20	0,27
0,06	0,33	0,28	0,36
0,08	0,42	0,36	0,46
0,1	0,51	0,44	0,55

Table 5-7: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Fast Reserve (degradation factor = 5) operation mode

FR degradation factor			10
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Expected value	Optimistic	Pessimistic
0,02	0,17	0,12	0,19
0,04	0,25	0,20	0,28
0,06	0,34	0,28	0,38
0,08	0,44	0,36	0,47
0,1	0,52	0,44	0,56

Table 5-8: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Fast Reserve (degradation factor = 10) operation mode

FR degradation factor			**20**
Electricity price [€/kWh]	Hydrogen price [€/Nm3]		
	Expected value	Optimistic	Pessimistic
0,02	0,18	0,13	0,21
0,04	0,27	0,21	0,30
0,06	0,36	0,29	0,39
0,08	0,45	0,38	0,49
0,1	0,54	0,46	0,58

Table 5-9: Deterministic Breakeven Hydrogen price depending on Electricity Price: Expected value, Optimistic and Pessimistic scenario. Fast Reserve (degradation factor = 20) operation mode

All these tables are conceived as the Table 5-1. Further discussion about the results are made in section 5.4.

5.2 HTSE

In this section the results of the brekeven capital cost analysis for the High Temperature Steam Electrolysis process are presented.

In Table 5-10 are reported the numerical results of the coupling between the HTSE Plant and a PWR (with an External Heat SuperHeater which provide addition heat to the 290 °C steam, burning Gas). In Table 5-11 are reported the numerical results of the coupling between the HTSE Plant and a VHTGR.

		SOEC + External Heater BREAKEVEN CAPITAL COST [k€/(Nm3/h)]: PWR+GAS											
		H_2 price [€/Nm3]				H_2 price [€/Nm3]				H_2 price [€/Nm3]			
		0.15	0.15	0.15	0.15	0.30	0.30	0.30	0.30	0.45	0.45	0.45	0.45
	Efficiency degradation [%/y]	2%	5%	10%	20%	2%	5%	10%	20%	2%	5%	10%	20%
EE price [€/kWh]	0.02	2.79	2.32	1.73	1.09	6.48	5.41	4.05	2.55	10.17	8.49	6.36	4.01
	0.04	1.37	1.12	0.82	0.52	5.06	4.21	3.13	1.97	8.75	7.29	5.44	3.43
	0.06	-0.09	-0.11	-0.13	-0.08	3.60	2.97	2.19	1.38	7.29	6.06	4.50	2.84
	0.08	-1.56	-1.35	-1.08	-0.67	2.13	1.73	1.24	0.79	5.82	4.82	3.55	2.24
	0.10	-3.00	-2.57	-2.01	-1.26	0.69	0.51	0.31	0.20	4.38	3.60	2.62	1.66

Table 5-10: SOEC + External Heater Breakeven Capital Cost, in the case of coupling between the HTSE Plant and a PWR, with the Steam Superheating provided by Natural Gas

		SOEC BREAKEVEN CAPITAL COST [k€/(Nm3/h)]: VHTGR											
		H_2 price [€/Nm3]				H_2 price [€/Nm3]				H_2 price [€/Nm3]			
		0.15	0.15	0.15	0.15	0.30	0.30	0.30	0.30	0.45	0.45	0.45	0.45
	Efficiency degradation [%/y]	2%	5%	10%	20%	2%	5%	10%	20%	2%	5%	10%	20%
EE price [€/kWh]	0.02	2.82	2.35	1.75	1.10	6.51	5.43	4.06	2.56	10.20	8.52	6.38	4.02
	0.04	1.29	1.05	0.76	0.48	4.98	4.14	3.07	1.94	8.67	7.22	5.39	3.40
	0.06	-0.29	-0.28	-0.26	-0.16	3.40	2.80	2.06	1.30	7.09	5.89	4.37	2.76
	0.08	-1.87	-1.62	-1.28	-0.80	1.82	1.47	1.03	0.66	5.51	4.55	3.35	2.12
	0.10	-3.43	-2.93	-2.28	-1,43	0.26	0.15	0.03	0.03	3.96	3.24	2.35	1.49

Table 5-11: SOEC Breakeven capital cost, in the case of coupling between the HTSE Plant and a VHTGR

It can be noticed that:

- almost all the corresponding cells of the two cases (PWR+NG and VHTGR) has very similar values, even though not identical. The weak difference is due to the additional cost of Natural Gas (for the Gas Burner, ESSH) present only in the first case. Anyway since the NG must provide just 72 MWth, the fuel consumption, and then its incidence are negligible.
  Looking at the DCF it can be seen that while the Electricity Night Costs range between 41 and 331 M€, the Natural Gas fuel cost is fixed at 4.5 M€;
- In the four columns of 0.15 €/Nm^3 H_2 price, for electricity prices above 6 c€/kWh the CAPEX reaches negative values;
- It is interesting, looking at the graphs in Figure 5-7, Figure 5-8, Figure 5-9, for negative CAPEX the curves' order is inverted and the 2% curve is more negative (so less convenient) than the others, which makes no sense. This effect is due to the slopes of the curves, so to their sensibility to the Electricity price variation.
  Since the O&M and Stack Replacement costs are expressed in percentage of the CAPEX, a negative CAPEX leads also to negative Stack Replacement costs, then a case in which the Stack Replacement are frequent (namely 20% efficiency degradation) paradoxically becomes the more convenient (according to the model). So the results can be considered acceptable until they positive of slightly negative;
- With the exception of the negative results, the values periodically follow a tendency, as could be expected: they decrease with the increasing of the electricity price, increase with the increasing of the hydrogen price, and again decrease with increasing the efficiency degradation;
- With low electricity prices the differences in the efficiency degradation maintain the curves distant, sign that if the electricity is cheap, the specific weight of the Stack Replacement in the cost breakdown is relevant. On the other hand, when the EP increases and especially when the curves are approaching the zero, they tend to focus at a point, sign that the differences in the efficiencies become less and less relevant if the energy source is too expensive.

Since the data listed in the Tables are very similar, only the results of the PWR+GAS case are represented in the graphics.
The cases that this study considers are: three for the hydrogen price, five for the electricity price, and four for the Efficiency degradation rate: 60 in total. Each graphic consists in four lines, showing the dependence of the Breakeven Capex from the Electric Price, for each level of efficiency degradation. Each of the three graphics (Figure 5-7, Figure 5-8, Figure 5-9) represents the result for a certain hydrogen price scenario.

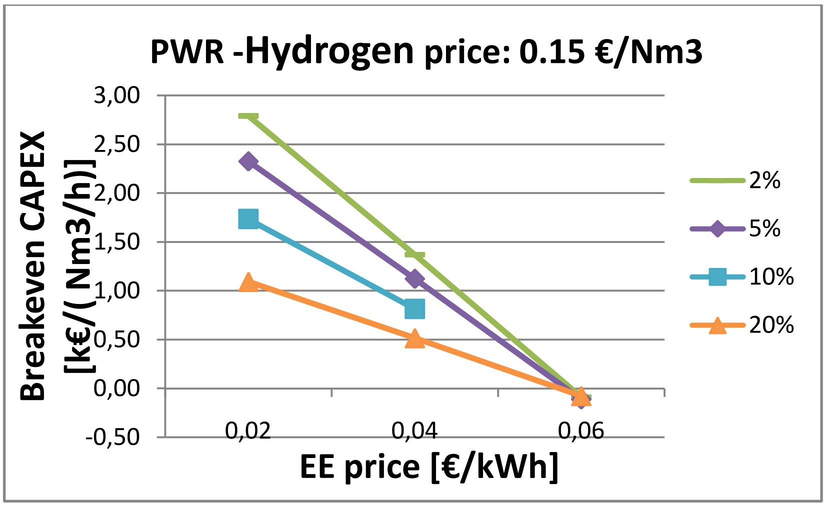


Figure 5-7: SOEC + External Steam SuperHeater breakeven cost. Hydrogen price scenario: Steam Methane Reforming production cost

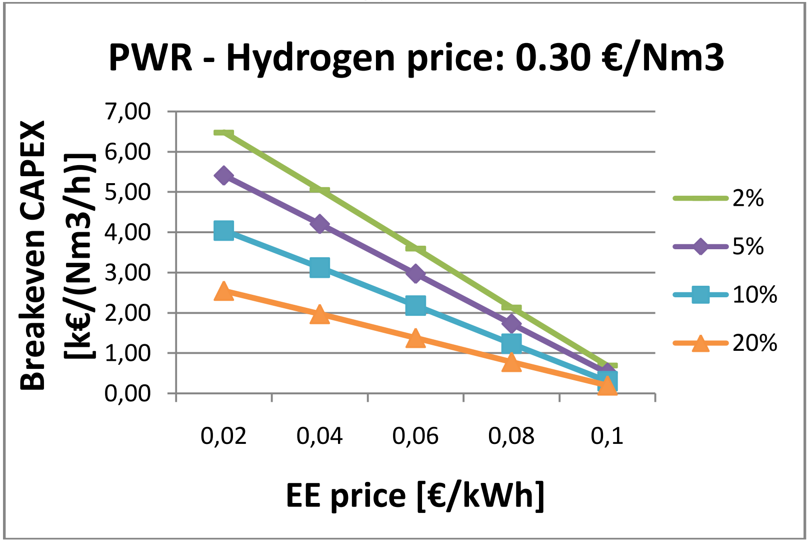


Figure 5-8: SOEC + External Steam SuperHeater breakeven cost. Hydrogen price scenario: moderately increased price.

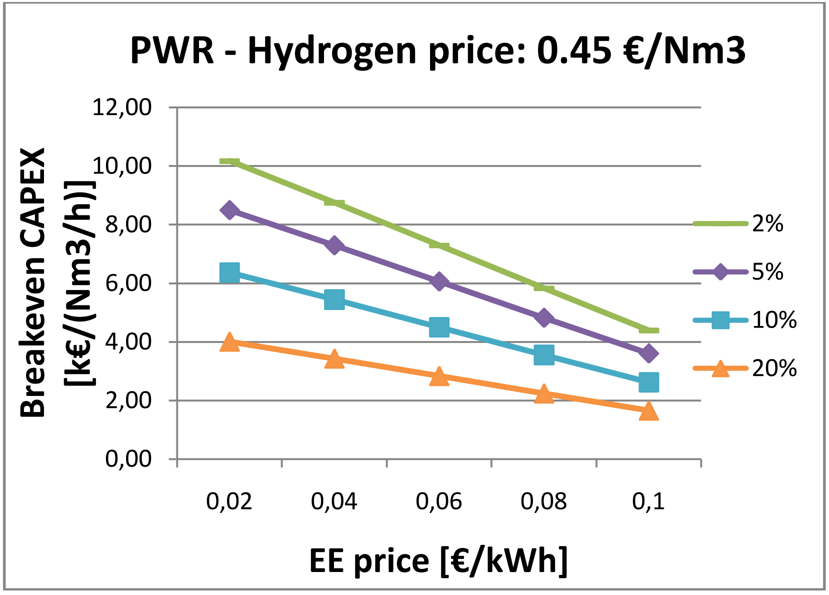


Figure 5-9: SOEC + External Steam SuperHeater breakeven cost. Hydrogen price scenario: widely diffused technology. High price.

5.3 SI cycle

In this section the results of the brekeven capital cost analysis for the Sulfur-Iodine process are presented.

In Table 5-12 are reported the numerical results of the coupling between the SI Plant and a VHTGR. The table is conceived in the same way of the HTSE case; the only difference is represented by the fourth raw, which represents the Fixed O&M costs (expressed in terms of % of the CAPEX) in place of the efficiency degradation rate (as it is in the HTSE case).

		SULFUR-IODINE BREAKEVEN CAPITAL COST [k€/(Nm3/h)]											
		H_2 price [€/Nm3]				H_2 price [€/Nm3]				H_2 price [€/Nm3]			
		0,15	0,15	0,15	0,15	0,3	0,3	0,3	0,3	0,45	0,45	0,45	0,45
	Fixed O&M [%]	2,5%	5,0%	7,5%	10,0%	2,5%	5,0%	7,5%	10,0%	2,5%	5,0%	7,5%	10,0%
EE price [€/kWh]	0,02	4,5	3,6	3,0	2,6	9,3	7,5	6,3	5,4	14,2	11,5	9,6	8,3
	0,04	2,9	2,3	1,9	1,7	7,7	6,2	5,2	4,5	12,6	10,2	8,5	7,3
	0,06	1,2	1,0	0,8	0,7	6,1	4,9	4,1	3,5	10,9	8,8	7,4	6,4
	0,08	-0,5	-0,4	-0,3	-0,3	4,4	3,6	3,0	2,6	9,3	7,5	6,3	5,4
	0,10	-2,1	-1,7	-1,4	-1,2	2,8	2,2	1,9	1,6	7,6	6,2	5,2	4,4

Table 5-12: Sulfur-Iodine Breakeven Capital Cost, according to hydrogen price, electric price and O&M cost scenarios

Most of the observations made for the HTSE case Tables remain valid here. In particular:

- In the four columns of 0.15 €/Nm^3 H_2 price, for electricity prices above 6 c€/kWh the CAPEX reaches negative values, and the most negative case in terms of fixed O&M(i.e. 10%) costs seems to be better than the 2.5 % case. Thus, for the same reasons explained in the previous section, the results can be considered acceptable until they positive of slightly negative;
- Also in this case, with the exception of the negative results, the values periodically follow a tendency, as could be expected: they decrease with the increasing of the electricity price, increase with the increasing of the hydrogen price, and again decrease with increasing the efficiency degradation;
- With low electricity prices the differences in the efficiency degradation maintain the curves distant, sign that if the electricity is cheap, the specific weight of the fixed O&M cost in the cost breakdown is relevant. On the other hand, when the EP increases and especially when the curves are approaching the zero, they tend to focus at a point, sign that the differences in the efficiencies become less and less relevant if the energy source is too expensive.

The graphics corresponding to Table 5-12, are shown in Figure 5-10, Figure 5-11, Figure 5-12:

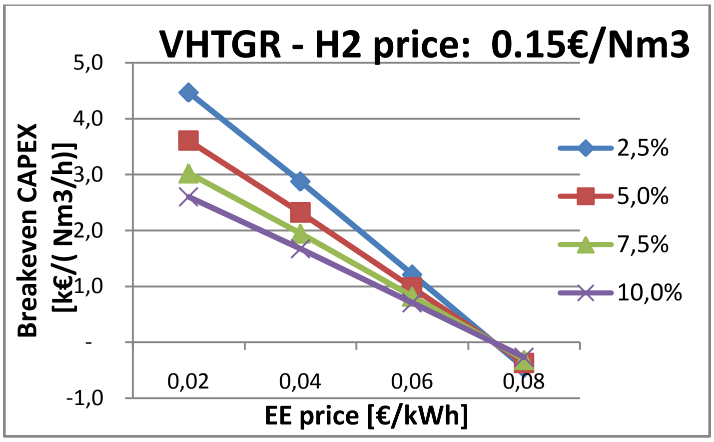


Figure 5-10: Sulfur Iodine plant (coupled with VHTGR) breakeven cost. Hydrogen price scenario: Steam Methane Reforming production cost.

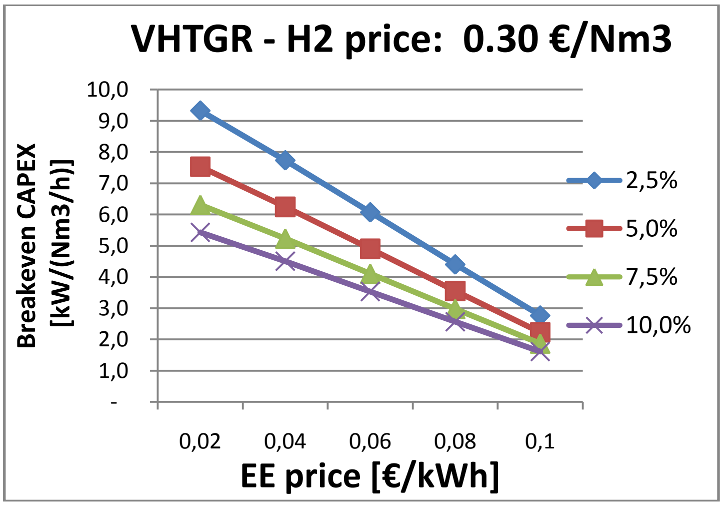


Figure 5-11: Sulfur Iodine plant (coupled with VHTGR) breakeven cost. Hydrogen price scenario: moderately increases price

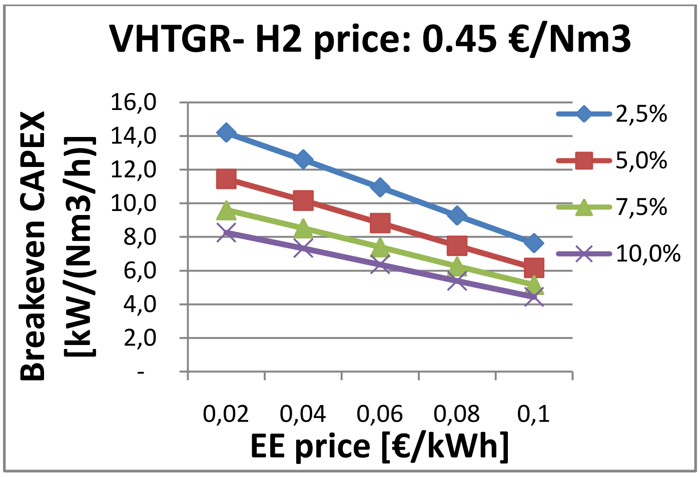


Figure 5-12: Sulfur Iodine plant (coupled with VHTGR) breakeven cost. Hydrogen price scenario: widely diffused technology. High price.

5.4 General discussion of results

After the presentation of all the numerical results from the economic analysis, and the explanation of the graphics, in this section the latter are commented.

5.4.1 AWE

The data from simulations of the breakeven hydrogen price in BC 8 and BC 12 case are interesting. While for current electricity prices (around 6 c€/kWh) BC 8 varies from 0.35 to 0.39 €/Nm^3, for the lowest electricity price scenario (2 c€/kWh) the BC 8 ranges between an optimistic value of 0.14 €/Nm^e to a pessimistic of 0.21. BC 12 does even better varying between 0.11 to 0.16, which is approximately the range of the Steam Methane Reforming production cost.

Nevertheless, the uncertainty of the deterministic analysis is too wide, leading to an excessive risk for an investment.

As expected, the Montecarlo simulation confirms to be a powerful method to strongly reduces the margin of uncertainty: for instance for an electricity price of 2 c€/kWh it forecast a BC 12 price ranging between 0.13 and 0.15 €/Nm^e.

In Figure 5-13 a comparison between all the considered operating strategies (including the four possible scenarios of efficiency degradation rate of the Fast Reserve operation) is made: the curves represent the percentage difference between the breakeven price calculated in each case and the one of the BC 8 case. The BC 8 curve is obviously constant and equal to zero. If a curve stands below 0, it is more profitable than the BC 8, since the breakeven price is inferior to its analogue of BC 8; otherwise it is less profitable.

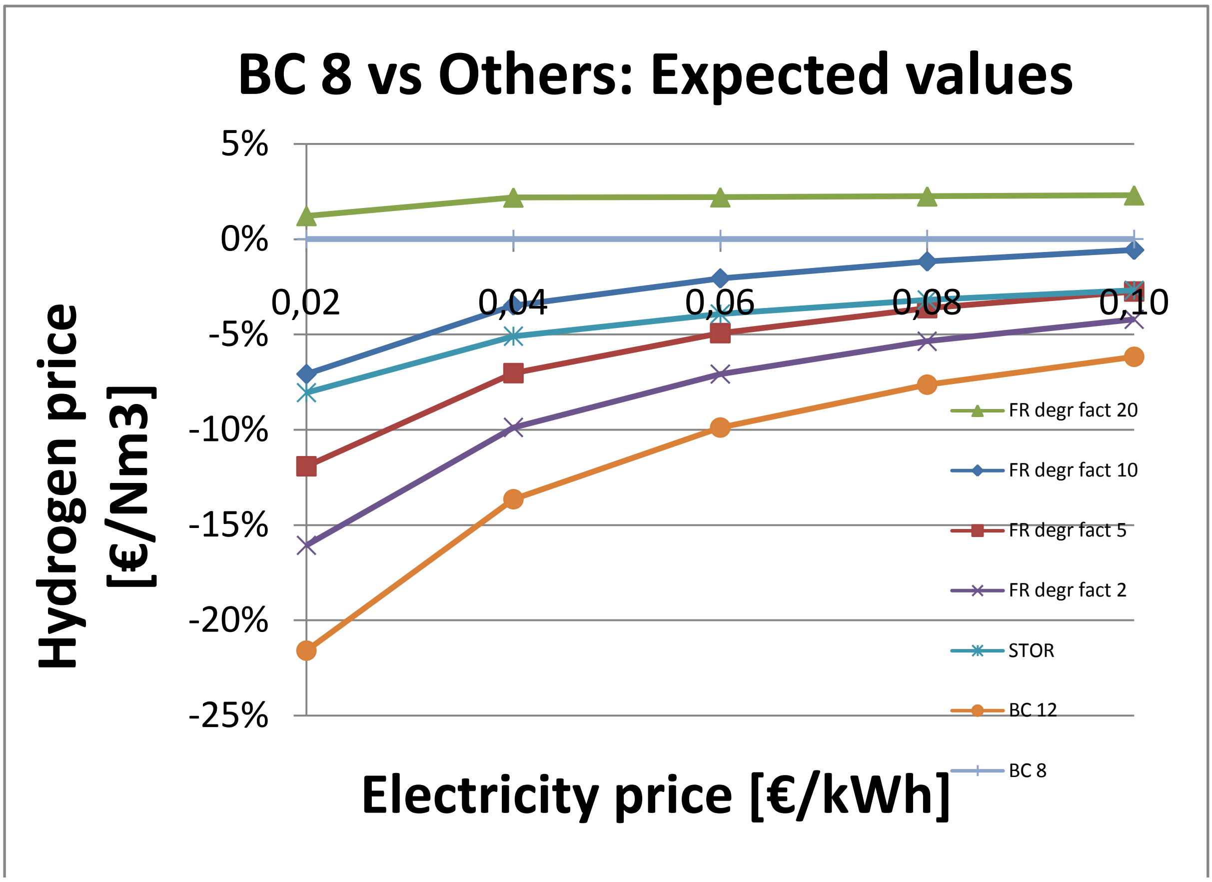


Figure 5-13: Comparison between all the cases: % difference between the Expected value of each case and the expected

Looking at the results of the deterministic breakeven hydrogen prices for the BC 8 and BC 12 it is possible to make the following considerations:

- For all the electricity prices, the BC 12 is more profitable than BC 8. This means than it actually is possible to perform Load Following with a WEP, but making the EZs work only for 8 hours represents an underutilization for the WEP. Even though considering a 12 hours day operation and 12 hours of night operation pushes this strategy at the limits of the definition of Load Following, it could be considered as an interesting option;
- The advantage of BC 12 with respect to BC 8 decreases (from -22% to -6%) when the electricity price increases. It can be expected that for an electricity price greater than 10 c€/kWh this trend is overturned;
- The STOR operation gives a weak extra value to the investment, probably due to its low additional revenues (1 M€/year) related to the availability and utilization payment;
- The FR operation is more interesting. If the efficiency degradation rate presents sufficiently low values (FR 2, FR 5) it present a significant advantage with respect to the BC 8 case (at 2c€/kWh FR 2 and FR 5 breakeven prices are respectively -16% and -12%), even though for high price of electricity this difference is mitigated. For

electricity prices higher than 4 c€/kWh the FR 10 presents no significant difference with respect to the BC 8. On the other hand, if the efficiency degradation rate is catastrophically high (FR 20) the Stack Replacement costs due to the malfunction of the 45 EZs operating this strategy overcome the additional revenues (from availability and utilization payment). This explains why the FR 20 curve is above the BC 8 one, regardless the electricity price.

Only tests conducted in laboratory can verify what is the real decrease in performances that the Fast Reserve operation causes.

5.4.2 HTSE and SI cycle

The data from the simulation of HTSE and SI can be treated together, since the considerations on them are the same.

The specific CAPEX of the WEP can be simply computed as the ratio of the Expected value of the Capital Cost and the plant of the size: in this way the value of 3.68 k€/(Nm^3/h) is obtained. All the breakeven CAPEX resulting from the simulations on HTSE and SI must be compared with this value.

Firstly, a fundamental clarification: even though the two cases of HTSE (PWR+NG and VHTGR) present the same breakeven CAPEX it does not mean that the two technologies are equivalent. Indeed, the values listed in tables Table 5-10 and Table 5-11 have different meanings:

- In the PWR+NG case, this is the maximum capex of a system including both the SOEC and the hypothesized steam superheating system (see 3.1). This means that the SOEC, alone, should cost less than the value reported in Table 5-10;
- In the VHTGR case, the extimated maximum capex includes only the SOEC.

As can be seen from Table 5-10, Table 5-11, and Table 5-12, if the hydrogen price remains low (0.15 €/Nm^3) both the HTSE and SI processes need to develop a very cheap technology (even cheaper than the current EZs, which are a mature technology) to represent an affordable investment; for electricity price above 6 c€/kWh, the breakeven CAPEX even reaches negative values. The 'goodness of the plant' (identified as the efficiency degradation rate for the SOEC and the O&M cost for the SI Plant) has negligible relevance in this hydrogen price scenario.

So the enhanced efficiency of the HTSE and SI with respect to the WE, even allowing to produce more hydrogen with the same power input, is not sufficient by itself to make the hydrogen from water splitting compete with the one from fossil sources.

With an increased hydrogen price, things change. For instance at 0.30 €/Nm^3 and 6 c€/kWh:

- the SOEC begins to be competitive, if it development achieves an efficiency degradation rate between 2 and 5%/year, otherwise it is not;

- the SI Plant stands in an advantage position.

Generally, the SI Plant is potentially competitive even for medium-high electricity prices if the hydrogen price reaches 0.30 €/Nm^3, almost regardless the value of O&M costs.
The SOEC becomes very profitable for high hydrogen prices (0.45),but only if efficiency degradation rate remains below the 5-10 %/year. In the case of 20 % of efficiency loss per year, which roughly means a stack lifetime of 2 years, the SOEC struggles to be competitive.

6 Conclusions & Future developments

Nuclear energy represents a proved opportunity to tackle most of the criticalities in the energy field, such as the growing energy demand, the greenhouse gas emissions, the scarcity of fossil fuels sources at cost-effective price, etc.

Anyway, there are several difficulties that the nuclear technology has to face in the future years.

Among them, there is the load following of the grid. Although nuclear energy has been mainly seen as a base load source, the evolving energetic portfolios and the recent limitations posed by institutions require even to nuclear plants to work in load following mode.

Nuclear technology is very capital intensive and almost all of its related costs are fixed or sunk. In order to save its economic affordability, a Nuclear Plant needs to maintain an high load factor; consequently, reducing the power production represents a great waste of resources.

Moreover, currently control rods and neutrons absorbers are inserted into the vessel to reduce the generated power. Following the grid by inserting negative reactivity into the core causes thermo-mechanical stresses in the primary loop.

Therefore, the idea on which this work is based is to address the excess (i.e. not required by the grid) thermal power produced during off-peak hours (i.e. the night) to an auxiliary, coupled with the NPP in a cogenerative layout.

The real challenge for this research field is to find a suitable industrial process. This process should possess certain characteristics:

- To be a technology that can be scaled up;
- Its feedstock should be common and available in sufficient quantity;
- The product should be sufficiently required by the market;
- Its characteristic in terms of temperature, power input and flexibility should be compatible with the Load Following operation.

The thermal applications are preferable in a medium-long term perspective, because they use hot steam before the heat is converted in electricity through a not-efficient conversion, but they are also much more difficult to realize.

In this work three possible by-products have been contemplated: diesel-like fuels (from plastic pyrolysis), wood pellets and hydrogen.

A preliminary analysis has been conducted in order to ascertain that the hypothetical plants would have been an annual energy request and a power input compatible respectively with the excess annual energy and power output (during the night) of a Nuclear Power Plant.

An approximated design has been sufficient to demonstrate that both for the plastic pyrolysis and wood pelletisation the feedstock procurement is a problem, because it is limited by non-technical factors.

More specifically, for the plastic pyrolysis plant to achieve a size large enough to absorb all the ‘excess energy’ produced by the Nuclear Plant, one third of the total annual plastic

waste produced in Europe should be collected and send to the plant. It is evident without doing any further calculation that this would be not an economical solution.
As for the wood pellet, the problem is represented by the procurement of the waste wood from the carpentries, situated in huge wood districts. Even though there is no evident technical limit in scaling up the pelletisation plant, a size of 1 Mtonne/year is considered by experts operating in this field, the maximum achievable.
Indeed, since the raw material used in these plants is waste wood of carpenters, which must be collected within a short distance (in order to avoid unsustainable transportation costs) these plants are placed at the centre of very large districts of woodworking, and their size is limited by the amount of waste material present, more than by other technical considerations. The calculations show that a 1 Mtonne/year plant would need approximately one fourth of the excess energy of the NPP, so also this idea has been abandoned.
Hydrogen has a theoretically infinite quantity of feedstock: the water. The market demand is one thousand of times the production correspondent to the energy provided by one Nuclear Plant. So the hydrogen is the only by-product surviving the first phase of the analysis.

Then, three different hydrogen production technologies, all of which obtain H_2 from water, have been investigated: water electrolysis, high temperature steam electrolysis and the Sulfur Iodine thermochemical cycle.
Among these, water electrolysis is the only one commercially developed. The other two are at different stages of research.
For different technology levels, different approaches of the techno-economic analysis have been adopted.

The obtained results can be classed in technical and economical. The main **technical results** are the following:

- The AWE, being an electric application, is a flexible technology that can easily be coupled with a NPP within a Load Following strategy, but the EZs require to be kept operate at 20% load during the day, in order to avoid an increase of the degradation velocity;
- The STOR operation does not present evident factors of unsustainability for the EZ, so it is not forecast a significant decrease in the efficiency with respect to the Base Case operation;
- On the other hand the FR operation puts a strain on the EZ, which however is capable to perform fast shut down and to recover rapidly. This operation would reasonably cause a relevant increase of the efficiency degradation;
- The HTSE, despite the high temperature, is mostly an electric application;
- The HTSE Plant can be coupled with a in a cogenerative design VHTGR, but these NPP are clearly not as common as PWR are. The coupling with and heating system made

of a PWR and a gas burner (which provides the steam superheating up to 850°C) is interesting from the energy balance standpoint, because the gas burner should supply just 72 MWth, over a HTSE Plant of 618 MWe input. Anyway its technical feasibility should be demonstrated;

- The Load Following with HTSE is more difficult, because it is not clear if a plant operating at 850 °C can easily adapt to periodical changes in power input. However the feasibility of this coupling cannot be excluded a priori. Moreover the modular nature of the plant (made by hundreds of SOECs) could help in this aspect;
- The SI Plant can definitely be coupled with a VHTGR in a cogenerative design. The coupling with and heating system made of a PWR and a NG burner is clearly not feasible since the NG heating system should provide at least 1,000 MWth, but probably even more. Moreover since currently the energy balances of the SI cycle are under R&D, it is impossible to forecast what part of the heating could be provided by the PWR. This suggests to abandon this idea.

Starting from these results and observations, the economic assessment of the three plants has been performed. The main **economic results** are the following**:**

- AWE main costs are represented by electricity. This, coupled with the great flexibility of this technology means that it can take a great advantage in working only during the off-peak hours;
- Hydrogen from AWE can be produced at relatively low prices until the electricity price is very low (2 c€/kWh);
- If electricity price is above 2 c€/kWh, the H_2 from water electrolysis cannot compete with the one from Steam Methane Reforming, unless a severe carbon tax is introduced;
- As expected, the Montecarlo simulation confirmed to be a powerful method to strongly reduces the margin of uncertainty on the hydrogen breakeven prices for BC 8 and BC 12 cases;
- For all the electricity prices, the BC 12 is more profitable than BC 8. Even though considering a 12 hours day operation and 12 hours of night operation pushes this strategy at the limits of the definition of Load Following, it could be considered as an interesting option;
- The STOR operation gives a weak extra value to the investment;
- The Fast Reserve operation gives a significant extra value to the investment until its efficiency degradation rate is low (2%/year);
- the SI Plant is potentially competitive (which means that its capital cost can be larger than the cost of a water EZ, still being economically profitable) even for medium-high electricity prices, if the hydrogen price reaches 0.30 €/Nm^3, almost regardless the value of O&M costs;
- The SOEC becomes very profitable for high hydrogen prices (0.45 0.30 €/Nm^3),but only if efficiency degradation rate remains below the 5-10 %/year.

However, before actually realizing Load Following with technologies such as SOEC and Sulfur Iodine Thermochemical Plant, not only technical but also regulations, licensing and public acceptance issues, must be faced.

Concerning the acceptability of current hydrogen costs, a fair comparison between the hydrogen from water electrolysis and the one from steam methane reforming cannot be made, because:

- The hydrogen from steam methane reforming has much lower purity than the one from WE, and is used mostly for industrial application (which does not require igh purity);
- The H_2 from WE has very high purity, so it is a shame to use it for industrial processes, while high purity is required by Fuel Cells.
  Essentially the hydrogen from WE is a product which needs a market: that would be provided by a wide diffusion of Fuel Cell Vehicles.

Consequently, further studies about this project can regard the following aspects:

- A detailed assessment of the optimal number of operating hours per day, studying its variation according to different electricity price distributions. Indeed, not only the Mean value of the EPD, but also the Standard Deviation (which influences the shape of the distribution) determines the optimal utilisation of the plant;
- Since the disposal of the great quantity of hydrogen produced in one year is complicated, it is possible to study the techno-economic feasibility of making the electrolysers work as fuel cells. In this way, the hydrogen is produced during the night , put in a tank for some hours and then re-converted in electricity during the peak hours. Several studies on this topic, including [139][140] , are already available in literature and can be taken as reference for this purpose.

Bibliography

[1] V. Nian and S. K. Chou, “The state of nuclear power two years after Fukushima – The ASEAN perspective,” *Appl. Energy*, vol. 136, pp. 838–848, Dec. 2014.

[2] C. K. Ebinger and S. Squassoni, “Industry and emerging nuclear energy markets,” in *Business and Nonproliferation*, Brookings Institution Press, 2011, pp. 66–119.

[3] International Energy Agency (IEA) Paris, “No Title,” in *World Energy Outlook 2010*, 2010.

[4] G. Davenport, C et Harris, “Obama to unveil tougher climate plan with his legacy in mind,” 2015.

[5] M. Landler, “US and China real climate accord after months of talks.”

[6] World Nuclear Association, “Nuclear Power share worldwide.” [Online]. Available: http://www.world-nuclear.org/info/Facts-and-Figures/Nuclear-generation-by-country/. [Accessed: 25-Aug-2015].

[7] World Nuclear Association, “World Nuclear Power Reactors & Uranium Requirements,” 2015. [Online]. Available: http://world-nuclear.org/info/Facts-and-Figures/World-Nuclear-Power-Reactors-and-Uranium-Requirements/#.UhKIb5I9-So.

[8] N. E. A.-O. for E. C. and D. NEA - OECD, “Technical and Economic Aspects of Load Followinf with Nuclear Power Plants,” 2011.

[9] C. Lombardi, *Nuclear Power Plant (Italian)*. 2009, p. 703.

[10] L. Pouret and W. J. Nuttall, “Can Nuclear Power Be Flexible ?,” pp. 1–25, 2008.

[11] P. Cappolani, “La chaudière des réacteurs à eau sous pression, France,” *Fr. EDP Sci.*, 2004.

[12] F. Pellegrino, “FLEXIBILITY OF NUCLEAR POWER :,” Politecnico di Milano, 2013.

[13] G. Locatelli, S. Boarin, F. Pellegrino, and M. E. Ricotti, “Load following with Small Modular Reactors (SMR): A real options analysis,” *Energy*, vol. 80, pp. 41–54, 2014.

[14] P. J. Gowin and T. Konishi, “Nuclear seawater desalination - IAEA activities and economic evaluation for southern Europe,” *Desalination*, vol. 126, pp. 301–307, 1999.

[15] H. Hidayatullah, S. Susyadi, and M. H. Subki, “Progress in Nuclear Energy Design and technology development for small modular reactors e Safety expectations , prospects and impediments of their deployment,” *Prog. Nucl. Energy*, vol. 79, pp. 127–135, 2015.

[16] S. Nisan and S. Dardour, “Economic evaluation of nuclear desalination systems,” *Desalination*, vol. 205, no. May 2006, pp. 231–242, 2007.

[17] IAEA, “Non-Electric Applications of Nuclear Power : Seawater Desalination , Hydrogen Production,” no. April, pp. 16–19, 2007.

[18] Iaea, “Advanced Applications of Water Cooled Nuclear Power Plants,” no. July, 2007.

[19] G. Alonso, R. Ramirez, and R. Castillo, “Process heat cogeneration using a high temperature reactor,” *Nucl. Eng. Des.*, vol. 280, no. June 1987, pp. 137–143, 2014.

[20] A. W. Paterson, R. A. Matzie, and R. Kuhr, “Beyond electricity - Nuclear process heat,” in *World Nuclear Association 32nd Annual Symposium*, 2007, pp. 53–60.

[21] H. Wang and K. T. Chuang, “EH2A cogeneration with nuclear power plant to sustain fuel production from oil sands bitumen,” in *8th World Congress of Chemical Engineering: Incorporating the 59th Canadian Chemical Engineering Conference and the 24th Interamerican Congress of Chemical Engineering*, 2009.

[22] D. Curtis and C. Forsberg, “Nuclear oil shale - Partnership opportunity for an expanded domestic SMR Market,” in *Transactions of the American Nuclear Society*, 2013, vol. 109, no. PART 2, pp. 2217–2220.

[23] H. Safa, “Heat recovery from nuclear power plants,” *Int. J. Electr. Power Energy Syst.*, vol. 42, no. 1, pp. 553–559, 2012.

[24] T. Muraleedharan Nair, “Profile on the Setting Up of Pyrolysis Plant for Plastic Wastes Conversion Into Industrial Diesel (Pyrolysis Oil), Gaseous Fuel & Carbon Black.”

[25] plasticseurope.org, “Plastics - The facts.”

[26] biomassmagazine.com, “List of North AmericaWood Pellet plants,” 2015. [Online]. Available: http://biomassmagazine.com/plants/listplants/pellet/US/.

[27] M. Balat, “Potential importance of hydrogen as a future solution to environmental and transportation problems,” *Int. J. Hydrogen Energy*, vol. 33, pp. 4013–4029, 2008.

[28] R. G. Lemus and J. M. Martínez Duart, “Updated hydrogen production costs and parities for conventional and renewable technologies,” *Int. J. Hydrogen Energy*, vol. 35, pp. 3929–3936, 2010.

[29] J. D. Holladay, J. Hu, D. L. King, and Y. Wang, “An overview of hydrogen production technologies,” *Catal. Today*, vol. 139, pp. 244–260, 2009.

[30] X. L. Yan and R. Hino, “Nuclear Hydrogen Production,” 2011.

[31] A. Shiroudi, S. R. H. Taklimi, S. A. Mousavifar, and P. Taghipour, “Stand-alone PV-hydrogen energy system in Taleghan-Iran using HOMER software: Optimization and techno-economic analysis,” *Environ. Dev. Sustain.*, vol. 15, pp. 1389–1402, 2013.

[32] G. Taljan, M. Fowler, C. Cañizares, and G. Verbič, “Hydrogen storage for mixed wind–nuclear power plants in the context of a Hydrogen Economy,” *Int. J. Hydrogen Energy*, vol. 33, no. 17, pp. 4463–4475, Sep. 2008.

[33] M. Gökek, “Hydrogen generation from small-scale wind-powered electrolysis system in different power matching modes,” *Int. J. Hydrogen Energy*, vol. 35, pp. 10050–10059, 2010.

[34] R. B. Gupta, *HYDROGEN FUEL Production Transport and Storage*. 2008.

[35] D. Shropshire, “Economic viability of small to medium-sized reactors deployed in future European energy markets,” *Prog. Nucl. Energy*, vol. 53, no. 4, pp. 299–307, 2011.

[36] Nordpoolspot, “Hourly UK electricity price.”

[37] F. Mueller-Langer, E. Tzimas, M. Kaltschmitt, and S. Peteves, “Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term,” *Int. J. Hydrogen Energy*, vol. 32, pp. 3797–3810, 2007.

[38] Eia: US Energy Information Administration, “Glossary.” [Online]. Available: http://www.eia.gov/tools/glossary/index.cfm?id=L.

[39] “The European Utility Requirement (EUR) document, Volume 2 revision C,” 2001.

[40] UK-EPR, “EPR: pre-construction safety report,” 2012.

[41] N. Todreas, *Nuclear Systems: volume I. Thermal Hydraulic Fundamentals*. 2012.

[42] M. D. Carelli, B. Petrovic, C. W. Mycoff, P. Trueco, M. E. Ricotti, and G. Locatelli, “Smaller sized reactors can be economically attractive,” *Soc. Fr. d’Energie Nucl. - Int. Congr. Adv. Nucl. Power Plants - ICAPP 2007, "The Nucl. Renaiss. Work.*, vol. 5, pp. 3140–3145, 2008.

[43] G. Locatelli and M. Mancini, “The role of the reactor size for an investment in the nuclear sector: An evaluation of not-financial parameters,” *Prog. Nucl. Energy*, vol. 53, no. 2, pp. 212–222, 2011.

[44] D. T. Ingersoll, “Deliberately small reactors and the second nuclear era,” *Prog. Nucl. Energy*, vol. 51, no. 4–5, pp. 589–603, 2009.

[45] C. W. Lapp and M. W. Golay, “Modular design and construction techniques for nuclear power plants,” *Nucl. Eng. Des.*, vol. 172, no. 3, pp. 327–349, 1997.

[46] D. Ingersoll, “Extending Nuclear Energy to Non-Electrical Applications,” 2014.

[47] N. Ghaffour, “The challenge of capacity-building strategies and perspectives 199 for desalination for sustainable water use in MENA,” *Desalin. Water Treat*, 2009.

[48] P. Asiedu-Boateng, “Modeling and simulation of cogeneration nuclear power plant for seawater desalination,” *Nucl. Eng. Des.*, 2012.

[49] I. S. Al-Mutaz, “Coupling of a nuclear reactor to hybrid RO-MSF desalination plants,” *Desalination*, vol. 157, no. January 2002, pp. 259–268, 2003.

[50] Y. H. Jung, Y. H. Jeong, J. Choi, A. F. Wibisono, J. I. Lee, and H. C. No, “Feasibility study of a small-sized nuclear heat-only plant dedicated to desalination in the UAE,” *Desalination*, vol. 337, no. 1, pp. 83–97, Mar. 2014.

[51] D. Curtis, C. Forsberg, M. McKellar, and E. Mattson, “A demonstration project coupling a small modular reactor with a hybrid nuclear renewable oil shale system,” in *International Congress on Advances in Nuclear Power Plants, ICAPP 2014*, 2014, vol. 3, pp. 2324–2333.

[52] EIA, “«International carbon dioxide emissions from the consumption of energy,».” [Online]. Available: http://www.eia.doe.gov/pub/international/iealf/tableh1co2.xls.

[53] D. Mojovic, “How to improve the economy of bioethanol production in Serbia,” *Renew. Sustain. Energy Rev.*, 2012.

[54] B. Wang, “CO2 bio-mitigation using microalgae,” *Appl. Microbiol. Biotechnol.*, 2008.

[55] A. A. Adenle, G. E. Haslam, and L. Lee, “Global assessment of research and development for algae biofuel production and its potential role for sustainable development in developing countries,” *Energy Policy*, vol. 61, pp. 182–195, Oct. 2013.

[56] S. Kumar, A. K. Panda, and R. K. Singh, “A review on tertiary recycling of high-density polyethylene to fuel,” *Resour. Conserv. Recycl.*, vol. 55, no. 11, pp. 893–910, 2011.

[57] T. Yoshioka, G. Grause, C. Eger, W. Kaminsky, and A. Okuwaki, “Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant,” *Polym. Degrad. Stab.*, vol. 86, pp. 499–504, 2004.

[58] a. Marcilla, M. I. Beltrán, and R. Navarro, “Evolution of products during the degradation of polyethylene in a batch reactor,” *J. Anal. Appl. Pyrolysis*, vol. 86, pp. 14–21, 2009.

[59] B. K. Sharma, B. R. Moser, K. E. Vermillion, K. M. Doll, and N. Rajagopalan, “Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags,” *Fuel Process. Technol.*, vol. 122, pp. 79–90, 2014.

[60] a. López, I. de Marco, B. M. Caballero, M. F. Laresgoiti, and a. Adrados, “Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor,” *Chem. Eng. J.*, vol. 173, pp. 62–71, 2011.

[61] A. Marcilla, M. D. R. Hernández, and Á. N. García, “Study of the polymer-catalyst contact effectivity and the heating rate influence on the HDPE pyrolysis,” *J. Anal. Appl. Pyrolysis*, vol. 79, pp. 424–432, 2007.

[62] “Polyflowcorp plastic pyrolysis plants.” [Online]. Available: http://www.polyflowcorp.com/. [Accessed: 22-Feb-2015].

[63] “Personal communication with academic or technical expert in the sector.”

[64] A. Uasuf and G. Becker, “Wood pellets production costs and energy consumption under different framework conditions in Northeast Argentina,” *Biomass and Bioenergy*, vol. 35, no. 3, pp. 1357–1366, 2011.

[65] S. Mani, “Economics of producing pellets from biomass,” *Appl. Energy*, 2006.

[66] P. S. Lam, S. Sokhansanj, X. Bi, C. J. Lim, and S. Melin, “Energy input and quality of pellets made from steam-exploded douglas fir (Pseudotsuga menziesii),” *Energy and Fuels*, vol. 25, pp. 1521–1528, 2011.

[67] P. S. Lam, “Steam Explosion of Biomass To Produce Durable Wood Pellets,” no. May, pp. 1–166, 2011.

[68] X. L. Yan and R. Hino, *Nuclear Hydrogen Production*. 2011, pp. 1–898.

[69] M. Felgenhauer and T. Hamacher, “State-of-the-art of commercial electrolyzers and on-site hydrogen generation for logistic vehicles in South Carolina,” *Int. J. Hydrogen Energy*, vol. 40, no. 5, pp. 2084–2090, 2015.

[70] R. B. Gupta, “HYDROGEN FUEL - Production, Transport and Storage,” 2008.

[71] L. Bertuccioll, A. Chan, D. Hart, F. Lehner, B. Madden, and E. Standen, “Study on development of water electrolysis in the EU,” no. February, 2014.

[72] M. MOMIRLAN and T. VEZIROGLU, “The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet,” *Int. J. Hydrogen Energy*, vol. 30, no. 7, pp. 795–802, Jul. 2005.

[73] S. Verhelst and T. Wallner, “Hydrogen-fueled internal combustion engines,” *Prog. Energy Combust. Sci.*, vol. 35, no. 6, pp. 490–527, Dec. 2009.

[74] C. College of the Desert, Palm Desert, “Hydrogen Fuel Cell Engines and Related Technologies,” 2001.

[75] N. Brandon, “An introduction to fuel cell technology and economics,” 1999.

[76] M. DELUCHI, “Hydrogen vehicles: an evaluation of fuel storage, performance, safety, environmental impacts, and cost,” *Int. J. Hydrogen Energy*, vol. 14, no. 2, pp. 81–130, 1989.

[77] K. Mazloomi and C. Gomes, “Hydrogen as an energy carrier: Prospects and challenges,” *Renew. Sustain. Energy Rev.*, vol. 16, no. 5, pp. 3024–3033, 2012.

[78] I. E. Agency, “Hydrogen Production and Storage,” *Energy*, vol. 13, pp. 392–392, 2006.

[79] R. G. Lemus and J. M. Martínez Duart, “Updated hydrogen production costs and parities for conventional and renewable technologies,” *Int. J. Hydrogen Energy*, vol. 35, no. 9, pp. 3929–3936, May 2010.

[80] Y. Yürüm, *Hydrogen energy system : production and utilization of hydrogen and future aspects*. NATO scientific affairs division, 1995.

[81] S. Trasatti, “Water electrolysis: who first?,” *J. Electroanal. Chem.*, vol. 476, pp. 90–91, 1999.

[82] J. M. ; H. D. T. B. M. Norbeck, *Hydrogen Fuel for Surface Transportation*. 1996.

[83] G. De Beni, *Hydrogen, key to the energy market*. Eurospectra, 1970, pp. 46–50.

[84] U.S. Department of Energy, “Fuel Cells and Infrastructure Technologies Program, Multi-Year Research, Development and Demonstration Plan,” 2007.

[85] M. Lewis, *Low Temperature Thermochemical Cycle Development*. Chicago, IL, 2003.

[86] K. Schultz, “Use of the modular helium reactor for H2 production.”

[87] K. Lieser, *Nuclear and Radiochemistry*. WILEY-VHC, 1997.

[88] Investing.com, “Natural Gas Price,” 2015. [Online]. Available: http://uk.investing.com/commodities/natural-gas.

[89] DOE, “FY 2008 Annual Progress Report.”

[90] J. R. Bartels, M. B. Pate, and N. K. Olson, “An economic survey of hydrogen production from conventional and alternative energy sources,” *Int. J. Hydrogen Energy*, vol. 35, no. 16, pp. 8371–8384, 2010.

[91] C. JORGENSEN and S. ROPENUS, “Production price of hydrogen from grid connected electrolysis in a power market with high wind penetration.,” *Int. J. Hydrogen Energy*, vol. 33, no. 20, pp. 5335–5344, Oct. 2008.

[92] M. Passolunghi, “Analisi e sviluppo di un elettrolizzatore in media pressione per la produzione di idrogeno e ossigeno,” 2010.

[93] B. Sørensen, *Hydrogen and Fuel Cells Emerging Technologies and Applications*. New York: Elsevier Academic Press, 2005, p. p.450.

[94] A. Ursúa, “Hydrogen Production From Water Electrolysis: Current Status and Future Trends,” *Proc. IEEE*, 2012.

[95] G. Turner, “No Title,” *Int. J. Hydrogen Energy*, pp. 379–407., 2008.

[96] Y. Shin, W. Park, J. Chang, and J. Park, “Evaluation of the high temperature electrolysis of steam to produce hydrogen,” *Int. J. Hydrogen Energy*, vol. 32, pp. 1486–1491, 2007.

[97] J.-P. Py and A. Capitaine, “Hydrogen Production By High Temperature Electrolysis of Water Vapour and Nuclear Reactors,” pp. 1–16, 2006.

[98] M. Ni, M. K. H. Leung, and D. Y. C. Leung, “Technological development of hydrogen production by solid oxide electrolyzer cell (SOEC),” *Int. J. Hydrogen Energy*, vol. 33, pp. 2337–2354, 2008.

[99] S. Singhal, *High Temperature Solid Oxide Fuel Cells: fundamentals, design, and applications*. 2003.

[100] Y. Arachi, “Electrical conductivity of the ZrO2–Ln2O3 (Ln=lanthanides) system,” *Solid State Ionics*, vol. 121, no. 1–4, pp. 133–139, Jun. 1999.

[101] S. R. Doenitz W, Schmidberger R, Steinheil E, “Hydrogen production by high temperature electrolysis of water vapour,” *Int. J. Hydrogen Energy*, 1980.

[102] N. Maskalick, “High temperature electrolysis cell performance characterization,” *Int. J. Hydrogen Energy*, 1986.

[103] Doenitz W, Schmidberger R, "Concepts and design for scaling up high temperature water vapor electrolysis," *Int. J. Hydrogen Energy*, 1982.

[104] R. Hino, K. Haga, H. Aita, and K. Sekita, "38. R&D on hydrogen production by high-temperature electrolysis of steam," *Nucl. Eng. Des.*, vol. 233, no. 1–3, pp. 363–375, Oct. 2004.

[105] B. Vad Mathiesen and I. Ridjan, "Technology Data for High Temperature Solid Oxide Electrolyser Cells , Alkali and Pem Electrolysers," pp. 1–16, 2013.

[106] Y. Bo, Z. Wenqiang, X. Jingming, and C. Jing, "Status and research of highly efficient hydrogen production through high temperature steam electrolysis at INET," *Int. J. Hydrogen Energy*, vol. 35, no. 7, pp. 2829–2835, 2010.

[107] C. Stoots, J. O. Brien, L. Moore-mcateer, and J. J. Hartvigsen, "High Temperature Solid- Oxide Electrolyzer 2500 Hour Test Results at the Idaho National," 2009.

[108] C. M. Stoots, J. E. O'Brien, K. G. Condie, and J. J. Hartvigsen, "High-temperature electrolysis for large-scale hydrogen production from nuclear energy - Experimental investigations," *Int. J. Hydrogen Energy*, vol. 35, no. 10, pp. 4861–4870, 2010.

[109] S. Fujiwara, S. Kasai, H. Yamauchi, K. Yamada, S. Makino, K. Matsunaga, M. Yoshino, T. Kameda, T. Ogawa, S. Momma, and E. Hoashi, "Hydrogen production by high temperature electrolysis with nuclear reactor," *Prog. Nucl. Energy*, vol. 50, pp. 422–426, 2008.

[110] M. Richards, "H2-MHR conceptual designs based on the sulphur–iodine process and high-temperature electrolysis," *Int. J. Hydrog. Prod. Appl.*, 2006.

[111] S. Kubo, H. Nakajima, S. Kasahara, S. Higashi, T. Masaki, H. Abe, and K. Onuki, "A demonstration study on a closed-cycle hydrogen production by the thermochemical water-splitting iodine - Sulfur process," *Nucl. Eng. Des.*, vol. 233, pp. 347–354, 2004.

[112] K. Kunitomi, X. Yan, T. Nishihara, N. Sakaba, and T. Mouri, "Jaea'S Vhtr for Hydrogen and Electricity Cogeneration : Gthtr300C," *Nucl. Eng. Technol.*, vol. 39, pp. 9–20, 2007.

[113] J. Norman, "Thermochemical water-splitting for hydrogen production," 1980.

[114] P. Trester, "Assessment and investigation of containment materials for the sulfur–iodine thermochemical water-splitting process for hydrogen production," 1981.

[115] K. Onuki, "IS process for thermochemical hydrogen production," 1994.

[116] S. Shiozawa, "Development status on hydrogen production technology using high-temperature gas-cooled reactor at JAEA," 2006.

[117] P. Pickard, "Sulfur–iodine thermochemical cycle," 2006.

[118] JAEA, "Status report 101 - Gas Turbine High Temperature Reactor (GTHTR300C)," 2011.

[119] E. R. Morgan, J. F. Manwell, and J. G. McGowan, "Opportunities for economies of scale with alkaline electrolyzers," *Int. J. Hydrogen Energy*, vol. 38, no. 36, pp. 15903–15909, 2013.

[120] J. Genovese, K. Harg, M. Paster, and J. Turner, "Current (2009) State-of-the-Art Hydrogen Production Cost Estimate Using Water Electrolysis Independent Review," *Analysis*, no. September, p. 51, 2009.

[121] National Grid, "What are Reserve Services." [Online]. Available: http://www2.nationalgrid.com/uk/services/balancing-services/reserve-services/.

[122] D. C. Invernizzi, "Using Real Options for the investment appraisal: the case of Energy Storage Systems in UK," Politecnico di Milano, 2015.

[123] National Grid, "Short Term Operating Reserves - Market Information," 2015. [Online]. Available: http://www2.nationalgrid.com/UK/Services/Balancing-services/Reserve-services/Short-Term-Operating-Reserve/Short-Term-Operating-Reserve-Information/. [Accessed: 23-Jan-2015].

[124] National Grid, "Fast Reserves market information." [Online]. Available: http://www2.nationalgrid.com/UK/Services/Balancing-services/Reserve-services/Fast-Reserve/Fast-Reserve-Information/.

[125] D. O. Akinyele and R. K. Rayudu, "Review of energy storage technologies for sustainable power networks," *Sustain. Energy Technol. Assessments*, vol. 8, pp. 74–91, Dec. 2014.

[126] H. Chen, T. N. Cong, W. Yang, C. Tan, Y. Li, and Y. Ding, "Progress in electrical energy storage system: A critical review," *Prog. Nat. Sci.*, vol. 19, no. 3, pp. 291–312, Mar. 2009.

[127] X. Luo, J. Wang, M. Dooner, and J. Clarke, "Overview of current development in electrical energy storage technologies and the application potential in power system operation," *Appl. Energy*, vol. 137, pp. 511–536, Oct. 2014.

[128] International Energy Agency (IEA) Paris, "Technology Roadmap: Energy Storage - Energy Technology Perspective," 2014.

[129] Department of Energy, "DOE Global Energy Storage Database," 2014. [Online]. Available: http://www.energystorageexchange.org/.

[130] EASE - European Association for Storage of Energy, "Energy Storage Database," 2015. [Online]. Available: http://www.ease-storage.eu/demonstrator.htm. [Accessed: 05-Dec-2014].

[131] J. O. Bockris and T. N. Veziroglu, "Estimates of the price of hydrogen as a medium for wind and solar sources," *Int. J. Hydrogen Energy*, vol. 32, no. 12, pp. 1605–1610, Aug. 2007.

[132] L. H. U.S. Department of the Interior - I.C. Watson, O.J.P. Morin, "Desalting Handbook for Planners," 2003.

[133] M. Centofante, "Heat removal systems and water consumption for IRIS and generation 3 nuclear power plants," 2009.

[134] D. Vivaldi, "Ethanol and Desalined Water Production with IRIS Nuclear Reactor," Politecnico di Milano, 2009.

[135] X. Yan, K. Kunitomi, T. Nakata, and S. Shiozawa, "GTHTR300 design and development," *Nucl. Eng. Des.*, vol. 222, no. April 2002, pp. 247–262, 2003.

[136] S. a. Sherif, F. Barbir, and T. N. Veziroglu, "Wind energy and the hydrogen economy-review of the technology," *Sol. Energy*, vol. 78, pp. 647–660, 2005.

[137] N. Hydrogen, "NEL A. Series Technical Data."

[138] a. G. Dutton, J. a M. Bleijs, H. Dienhart, M. Falchetta, W. Hug, D. Prischich, and a. J. Ruddell, "Experience in the design, sizing, economics, and implementation of autonomous wind-powered hydrogen production systems," *Int. J. Hydrogen Energy*, vol. 25, pp. 705–722, 2000.

[139] National grid, "Firm Fast Reserve Post Assessment Tender Report - Mar 2014," no. May, p. 2014, 2014.

[140] R. Brealey, *Principles of Corporate Financial*, Sixth. 2000.

[141] P. Kodukula, *Project Valuation Using Real Options, A Practitioner's Guide*. 2006.

[142] M. A. Brach, *Real Options in practice*. 2003.

[143] R. Neufville, *Flexibility in Engineering Design*. 2009.

[144] A. Ursúa, I. San Martín, E. L. Barrios, and P. Sanchis, "Stand-alone operation of an alkaline water electrolyser fed by wind and photovoltaic systems," *Int. J. Hydrogen Energy*, vol. 38, pp. 14952–14967, 2013.

[145] C. Mansilla, J. Louyrette, S. Albou, C. Bourasseau, and S. Dautremont, "Economic competitiveness of off-peak hydrogen production today – A European comparison," *Energy*, vol. 55, pp. 996–1001, Jun. 2013.

[146] F. Gutiérrez-Martín and I. Guerrero-Hernández, "Balancing the grid loads by large scale integration of hydrogen technologies: The case of the Spanish power system," *Int. J. Hydrogen Energy*, vol. 37, pp. 1151–1161, 2012.

List of the consulted experts:

Reference number	Name	Company/University	Item	Communication mean	Date
1.	Tiziano Favarelli	Politecnico di Milano	Plastic pyrolysis	Phone call	16/3/15
2.	Alexander Lopez	Bilbao University	Plastic pyrolysis	email	27/2/15
3.	Guido Grause	Tohoku Univerisyt	Plastic pyrolysis	email	19/2/15
4.	Stefano Consonni	Politecnico di Milano	Candidates Auxiliry plants	Phone call	10/3/15
5.	Luca Lietti	Politecnico di Milano	Candidates Auxiliry plants	Phone call	10/3/15
6.	Abby Saddawy	University of Lincoln	Wood Pellettization	Phone call	3/3/15
7.	Scot Linkletter	Maine Woods Pellet	Wood Pellettization	email	27/4/15
8.	Massimo Rosi	EX employee: Italiana Pellets	Wood Pellettization	Phone call	11/3/15
9.	Paolo Giarda	Italiana Pellets	Wood Pellettization	Phone call	18/3/15
10.	Jari Hiltunen	ANDRITZ	Steam Exploded Pellets	email	4/3/15
11.	Stefano Campanari	Politecnico di Milano	Water Electrolysers	email	12/3/15
12.	Luca Nobili	Politecnico di Milano	Water Electrolysers	Phone call	16/3/15
13.	Massimo Santarelli	Politecnico di Torino	Water Electrolysers	Phone call	9/3/15
14.	Markus Felghenauer	BMW	Water Electrolysers	email	2/4/15
15.	Henning G. Langas	NEL Hydrogen	Water Electrolysers	email	7/8/15
16.	Eric Dabe	NEL Hydrogen	Water Electrolysers	email	13/5/15; 27/8/15
17.	Luca Bertuccioli	E4tech	Water Electrolysers	email	15/5/15
18.	David Elia	Idroenergy	Water Electrolysers	Phone call	27/5/15
19.	Franz Lehner	E4tech	Water Electrolysers	email	15/5/15
20.	Fernando Gutierrez	Universidad Politecnica de Madrid	Water Electrolysers	email	3/3/15
21.	Roel De Mayer	Hydrogenics	Water Electrolysers	email	13/3/15
22.	Enrico Febbraro	Linde	Hydrogen market	email	8/6/15
23.	Paul Marotta	University of Tennessee	HTSE	email	4/8/15
23.	Steve Miller	UK National Grid	Electricity Reserve market in UK	email	24/8/15

Table 6-1: List of the consulted experts

List of acronyms:

Acronym	Meaning
ABWR	Advanced Boiling Water Reactor
AEZ	Alkaline Elecrolyzer
AWE	Alkaline Water Electrolysis
BC	Base Case
BM	Balancing Mechanism
BWR	Boiling Water Reactor
CAES	Compressed Air Energy Storage
CAPEX	Capital Expenditure
CCGT	Combined Cycle Gas Turbine
DCF	Discounted Cash Flow
EE	Electric Energy
EfD	Efficiency Degradation
EP	Electricity Price
EPD	Electricity Price Distribution
EPR	European Pressurized Reactor
ESS	Energy Storage Systems
ESSH	External Heat SuperHeater
EZ	Electrolyzer (Electrolyser)
FR	Fast Reserve
GA	General Atomic
GB	Great Britain
GHG	Greenhouse Gas
GT	Gas Turbine
HTH	High Temperature Heating
HTSE	High Temperature Steam Electrolysis
IEA	International Energy Agency
IHX	Intermediate Heat Exchanger
INL	Idaho National Laboratory
IRIS	International Reactor Innovative and Secure
IRR	Internal Rater of Return
JAEA	Japan Atomic Energy Agency
LCOE	Loevelized Cost of Electricity
LET	Linear Energy Transfer
LF	Load Following
LHV	Lower Heating Value
LR	Large Reactor
LTH	Low Temperature Heating
LWR	Light Water Reactor
MC	MonteCarlo

NG	Natural Gas
NPP	Nuclear Power Plant
NPV	Net Present Value
O&M	Operation & Maintenance
OPEX	Operational Expenditure
PBMR	Pebble Bed Modular Reactor
PEM	Proton Exchange Membrane
PHS	Pumped Hydroelectric Storage
PV	Photovoltaic
PWR	Pressurized Water Reactor
SI	Sulfur-Iodine
SMR	Small Modular Reactor
SOEC	Solid Oxide Electrolyser Cell
STOR	Short Term Operating Reserve
SWRO	Seawater Reverse Osmosis
TD	Thermodynamic
U.S. DOE	US Department of Energy
UCTE	Union for the Coordination of the Trasmission of Electricity
UK	United Kingdom
VHTGR	Very High Temperature Gas Reactor
WACC	Weighted Average Cost of Capital
WE	Water Electrolysis
WEP	Water Electrolysis Plant
YSZ	Yttria-stabilized Zirconia

Table 6-2: List of acronyms