Chloride family of cycles

Process principle

Hybrid Chlorine cycle

(1)	$Cl_{2(g)} + H_2O_{(g)} \rightarrow 2HCl_{(g)} + ½O_{2(g)}$	850 °C
(2)	$2HCl_{(g)} \rightarrow H_{2(g)} + Cl_{2(g)}$ *electrolysis*	75 °C

Iron-chlorine cycle

(1)	$3FeCl_{2(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + 6HCl_{(g)} + H_{2(g)}$	925 °C
(2)	$Fe_3O_{4(s)} + 8HCl_{(g)} \rightarrow FeCl_{2(s)} + 2FeCl_{3(s)} + 4H_2O_{(g)}$	125 °C
(3)	$2FeCl_{3(s)} \rightarrow 2FeCl_{2(s)} + Cl_{2(g)}$	425 °C
(4)	$Cl_{2(g)} + H_2O_{(g)} \rightarrow 2\ HCl_{2(g)} + ½O_{2(g)}$	850 - 925 °C

Vanadium-chlorine cycle

(1)	$2VCl_{2(s)} + 2HCl_{(g)} \rightarrow 2VCl_{3(s)} + H_{2(g)}$	120 °C
(2)	$4VCl_{3(s)} \rightarrow 2VCl_{2(s)} + 2VCl_{4(g)}$	750 °C
(3)	$2VCl_{4(l)} \rightarrow 2VCl_{3(s)} + Cl_{2(g)}$	200 °C
(4)	$Cl_{2(g)} + H_2O_{(g)} \rightarrow 2\ HCl_{(g)} + ½O_{2(g)}$	850 - 925 °C

Cerium-chlorine cycle

(1)	$2CeO_{2(s)} + 8HCl_{(g)} \rightarrow 2CeCl_{3(s)} + Cl_{2(g)} + 4H_2O_{(g)}$	110 °C
(2)	$2CeCl_{3(s)} + 4H_2O_{(g)} \rightarrow 2CeO_{2(s)} + 6HCl_{(g)} + H_{2(g)}$	925 °C
(3)	$Cl_{2(g)} + H_2O_{(g)} \rightarrow 2HCl_{(g)} + ½\ O_{2(g)}$	850 - 925 °C

Hydrid copper-chlorine cycle

(1)	$2CuCl_{2(s)} + H_2O_{(g)} \rightarrow Cu_2OCl_{2(s)} + 2HCl_{(g)}$	425 °C
(2)	$Cu_2OCl_{2(s)} \rightarrow 2CuCl_{(l)} + ½O_{2(g)}$	530 °C
(3)	$4CuCl_{(s)} \rightarrow 2CuCl_{2(aq)} + 2Cu_{(s)}$ *electrochemical*	25 - 80 °C
(4)	$2CuCl_{2(aq)} \rightarrow 2CuCl_{2(s)}$	> 100 °C
(5)	$2Cu_{(s)} + 2HCl_{(g)} \rightarrow 2CuCl_{(l)} + H_{2(g)}$	425 - 475 °C

Simple screening of these processes, based on maturity and evaluation of the cycle technical challenges, has identified the ***hybrid copper-chlorine cycle*** *as currently the most promising of the chloride family.*[1,2]

Hybrid copper-chlorine cycle

Heat source: Nuclear or Solar.[5,6]

Materials: High temperature alloys with coatings of silicon based ceramics.[7]

Cost evaluation: Projected from \$ 3.00 to 3.95 /kg H_2.[6]

Cycle	Advantages[1,2]
Hybrid Cl_2	Simple principle, known technology in HCl electrolysis, two step separation.
Fe - Cl	Low costs, chemistry of iron oxides well known.
V - Cl	High projected efficiency.
Ce - Cl	The cycle can be partially carried out in the aqueous phase, allowing optimisation of operating temperature.[3]
Cu - Cl	Low maximum temperature, all reactions demonstrated at laboratory scale, safe, abundant and inexpensive intermediate chemicals, no catalyst needed for thermal reactions,[4] international support.

Cycle	Challenges[1,2]
Hybrid Cl_2	Limited equilibrium reaction (60 %) at 850 °C, new technology required to improve efficiency in reverse Deacon reaction (same challenge for the other cycles except for Cu-Cl cycle). HCl/H_2 and Cl_2/H_2O separation.
Fe - Cl	Heat management during (3), competition in product formation (dimerization of $FeCl_3$ into Fe_2Cl_6).
V - Cl	Unknown thermodynamic data for vanadium oxides, slow kinetic, separation methods.
Ce - Cl	Low efficiency, slow kinetics (if gas-solid reaction).
Cu - Cl	Development of the electrochemical reaction. H_2O/HCl separation in (1), H_2/HCl separation in (5), incomplete reaction (5).

Cycle	Expected efficiency[1,2]
Hybrid Cl_2	34 - 35 %
Fe - Cl	18.5 %
V - Cl	31 - 46 %
Ce - Cl	20.9 %
Cu - Cl	15[14] - 43 %

Flow-sheet

The current version of the Cu-Cl cycle involves five steps[8]:

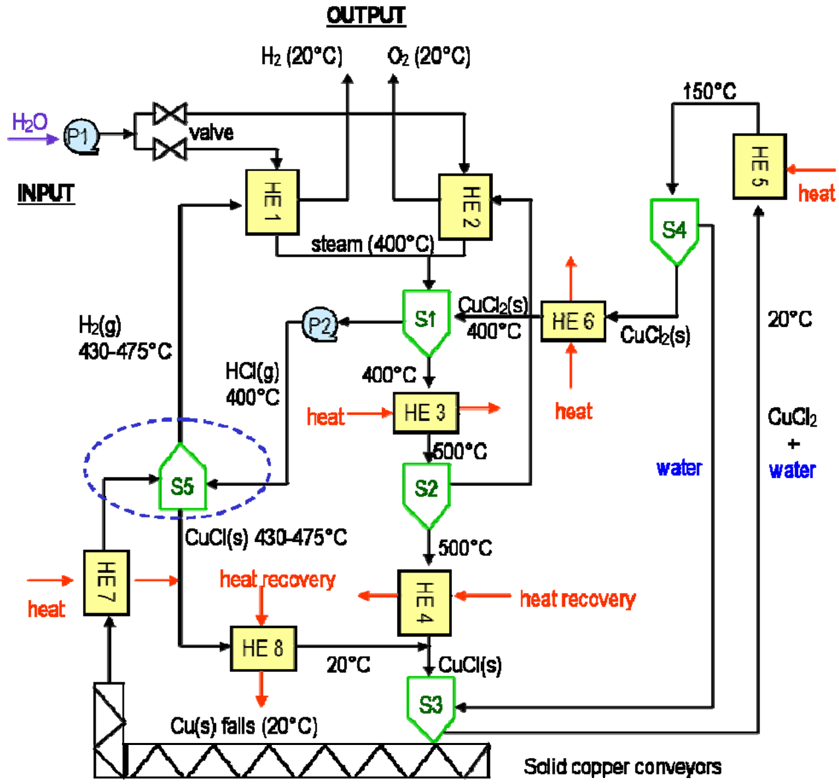
(S1) Hydrolysis step
$2CuCl_2 + H_2O \rightarrow Cu_2OCl_2 + 2HCl$

(S2) Oxygen production
$Cu_2OCl_2 \rightarrow 2CuCl + ½O_2$

(S3) Copper (Cu) production
$4CuCl \rightarrow 2CuCl_2 + 2Cu$

(S4) Drying
$2CuCl_{2(aq)} \rightarrow 2CuCl_{2(s)}$

(S5) Hydrogen production
$2Cu + 2HCl \rightarrow 2CuCl + H_2$



- Liquid water at ambient temperature enters the cycle. After being compressed by **P1**, it passes through heat exchangers (**HE1, HE2**) where it is evaporated. The temperature is increased to 400 °C using heat obtained by cooling the H_2 and O_2 gases before they exit the process.[9]
  Steam and $CuCl_{2(s)}$ at 400 °C from the dryer enter the fluidized bed (**S1**). This endothermic hydrolysis reaction is considered the most challenging one because of the competing reaction (thermal decomposition of $CuCl_{2(s)} \rightarrow 2CuCl_{(s)} + Cl_{2(g)}$) and the need for excess water.[6,2] . $HCl_{(g)}$ is then compressed by **P2**.

- In (**S2**), an endothermic chemical reaction takes place: Cu_2OCl_2 heated to 530 °C, produces O_2 and $CuCl_{(l)}$. The $CuCl_{(l)}$ is solidified by cooling to 20 °C.

- The CuCl produced from (S2) and (S5) endothermically reacts at 20 °C. In this reaction (**S3**), water acts as a catalyst and does not react with other compounds. This step is cost challenging since it involves an electrolysis reaction to produce $Cu_{(s)}$ and $CuCl_{2(l)}$. $Cu_{(s)}$ exits on a conveyer.

- The aqueous $CuCl_2$ stream is preheated to 150°C and transferred to the flash dryer (**S4**), to produce $CuCl_{2(s)}$ which goes to the electrochemical cell (S3) or enters (S1) after its temperature has increased.

- The hydrogen generation (**S5**) is a heterogeneous exothermic and reversible reaction and takes place at a steady state. The reaction temperature is above 425 °C (melting point of the CuCl) to avoid the passivation of the Cu metal surface.[9]

Experiments and existing prototypes

The Cu-Cl cycle has been identified by Atomic Energy of Canada Limited (AECL) as a promising cycle for H_2 production.[10]
Current collaboration between UOIT (University of Ontario Institute of Technology), AECL and the Argonne National Laboratory focuses on enabling technologies for the Cu-Cl cycle, through a International Nuclear Energy Research (I-NERI).[8]
A research team, led by UOIT, has built a laboratory demonstration at a scale of **5 kg H_2/day**.[10]
The scale-up of a multiphase reactor has been examined.[11] The different steps are::

The hydrolysis

For this reaction, a fixed bed reactor design is not effective.[12] Instead, cupric particles react with superheated steam in fluidized bed reactor.[10]

The Oxygen production step

This reaction occurs in a fixed bed or moving bed reactor. A quenching cell can be used for molten Cu-Cl transformation to the $Cu\text{-}Cl_{(s)}$ required for the electrochemical step[5].

The Electrolytic reaction

This reaction has been demonstrated by AECL. Improved performance (500 mA/cm^2 at 0.5 V) and decreased cost ($ 2500/m^2) are the primary challenges for electrolysis scale-up.[6]

An adaptation of silver-refining technology based on the Moebius cell is possible. However, this technology is too expensive and energy intensive, it could be used as a basis of an alternative equipment.[7,8]

Drying

To improve the evaporation process, a new method is being evaluated. It consists of pressurizing the liquid stream sufficiently to atomize droplets through a pressure-reducing nozzle in the spray system.[7]

This spray drying system can be used instead of separate drying and hydrolysis processes.[11]

Hydrogen production

In the reactor unit, copper particles enter the mixing chamber, descend along an inclined bed and meet HCl to produce CuCl.[7] A sedimentation vessel is used to separate unreacted copper particles. Afterwards, particles return back to the reaction chamber.

Simultaneously, HCl passes through the chamber to generate H_2 in a second exit stream. To separate unreacted HCl from the H_2 produced, the gas is absorbed by an absorption tower.[11]

Description of heat sources

The maximum cycle temperature (530 °C) allows the use of multiple and proven heat sources.[4] Several types of nuclear reactors can be used, such as the Supercritical Water Reactor (Generation IV) developed in Canada, the lead cooled reactor, or the high temperature gas reactor.[5]

Solar heat can be provided using tower technology.[6]

Materials

Some components, such as heat exchangers require new materials to allow economic viability in the extreme operating conditions of high temperature corrosive fluids. High temperature alloys with coatings of silicon based ceramics appear promising in this regard, but their thermal behaviour and surface interactions in high-temperature multiphase conditions must be studied.[7]

Expected efficiency

A key advantage is the cycle's ability to utilize external waste heat from power plants, for various thermal processes within the cycle. Moreover, up to 40 % of the heat required by Cu-Cl cycle can be provided through internal processes within the cycle.[8]

Concerning the cycle's efficiency, Aspen plus™ simulation has indicated potentially up to 53 % thermal efficiency, but only 43 % when losses due to engineering equipment operation are included.[5,8]

Cost evaluation

A conceptual process design has been developed to produce 125 MT of H_2/day. The estimated cost of producing H_2 is $ 3.30/kg.

The sensitivity analysis show that the cost of H_2 can range from $ 3.00 to 3.95/kg.

The cost is more sensitive to the plant capital cost, the operating factor and the cost of energy (both electrical and thermal) than the size of the labour force and the amount of equity financing.[6]

According to recent projections based on the H2A Central Production Tool, hydrogen production costs **using solar energy** has been predicted at $ 4.30 in 2015, and $ 2.82 in 2025.[13] Hydrogen production costs are tightly related to techno-economic models.

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