

## Stepping Towards Decarbonisation: ONGC Energy Centre strides in Green Hydrogen Production

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### Abstract

Government of India has initiated several National missions towards Research, Development and Demonstration (RD&D) activities that provide energy security to the nation (India Country Status Report on Hydrogen and Fuel Cells, 2020). With respect to the India's commitment to a net zero emissions target by 2070, National Hydrogen Energy Mission (NHEM) was launched by the government in August 2021 aiming to provide a comprehensive action plan for establishing a Green Hydrogen ecosystem and catalyzing a systemic response to the opportunities and challenges of this sunrise sector. As India has set its sight on becoming energy independent by 2047 and achieving Net Zero by 2070, India is gearing up for meeting imminent energy transition with the help of renewables where water and hydrogen are the lead players (NHEM, 2023).

Recently, India has published its Green Hydrogen Policy in February 2022 as first initiative under the National Hydrogen Mission to promote production and utilization of green hydrogen and green ammonia (Green Hydrogen Policy, 2022). Both the Government and public sectors in India are supporting RD&D projects on different aspects of hydrogen economy including production, storage and utilization for stationary, power generation and for transport applications.

In line with the on-going rapid developments in encouraging and promoting hydrogen economy by the Government of India, ONGC Energy Centre (OEC) has initiated RD&D activities for indigenous development of Green Hydrogen Economy. This article enlightens the advances made by OEC in developing Green Hydrogen Eco-system by following a collaborative consortium mode with various national Centres of excellence with focus on large scale green hydrogen generation by cost

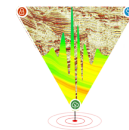
effective indigenous technology along with its utilization in conjunction with CO<sub>2</sub> to provide an integrated solution to reduce carbon foot print during and beyond the energy transition leading to net zero realization.

### Introduction

Hydrogen being clean, non-polluting, renewable, and versatile source is considered as a promising energy carrier. It's abundance in different forms, high energy density, clean combustion, and convertibility into electricity or useful chemicals makes Hydrogen more popular and globally accepted (India Country Status Report, 2020). It can be produced from a variety of feed stocks using diverse pathways and finds application in different industrial sectors viz. chemical, petrochemical, agricultural, metallurgy, food processing, plastics, electronic and energy (Martinez-Burgo et al, 2021). As of now, 95% of hydrogen produced around the world is 'Grey hydrogen', produced from fossil fuels. However, 'Green Hydrogen' can be produced by breaking down water molecules (H<sub>2</sub>O) into oxygen (O<sub>2</sub>) and hydrogen (H<sub>2</sub>) by electrolysis or thermochemical splitting, provided the electricity used to power the process is entirely from renewables.

### Green Hydrogen by Thermochemical Water Splitting

Water being the abundant resource on the earth has attained more importance in the Green Hydrogen Economy. However, the method of hydrogen production decides the environmental impact and energy efficiency. Direct thermal decomposition of water into hydrogen and oxygen requires temperatures in excess of 2500°C (Chao, 1975). However, thermochemical water splitting/decomposition, or more commonly called



“thermochemical cycles” is an emerging and promising technology for large-scale production of hydrogen due to reduced temperature requirement. A thermochemical cycle uses two or more intermediate compounds in a sequence of chemical and physical processes to split water molecules into hydrogen and oxygen at much lower temperature than thermal decomposition. The intermediate compounds are recycled internally, creating a closed loop that consumes only water and produces hydrogen and oxygen. These possess many advantages such as no requirement of product gas separation, moderate operating temperatures between 600 and 1200K, minimum or very low power input requirement and can be solar and nuclear driven. They use both thermal energy and electricity through a sequence of thermochemical and electrochemical reactions.

Although over 200 possible thermochemical cycles have been proposed in the past (McQuillan et al., 2002 and Lewis et al., 2006), very few have progressed beyond concepts and theories to working demonstrations showing practical feasibility of the processes. In recent years, numerous organizations and researchers worldwide i.e. from USA (General Atomics, Savannah River National Laboratory, Argonne National Laboratory (ANL)), Canada (University of Ontario Institute of Technology (UOIT), Atomic Energy of Canada Limited (AECL), UNENE (University Network of Excellence in Nuclear Engineering), Japan (Japan Atomic Energy Agency, JAEA), France (Commissariat à l’Energie Atomique, CEA), Korea (KAERI), South Africa, China, and others are focusing particularly on the iodine-sulfur (I-S), hybrid sulfur and copper-chlorine (Cu-Cl) cycles. Currently, these cycles are at different stages of development globally and are yet to be commercially proven (Norman et al., 1982, Naterer et al., 2011).

#### **Research, Development and Demonstration (RD&D) by ONGC Energy Centre (OEC) in Green Hydrogen Production**

ONGC Energy Centre (OEC) has been developing highly efficient clean and green indigenous hydrogen generation technologies using thermochemical water splitting from a concept to commercialization using renewable, thermal power and water. Among various possible options of thermochemical cycles with regard to the choice of likely process routes for

development, OEC has chosen two processes i.e. Copper-Chlorine (Cu-Cl) cycle and Iodine-Sulfur (I-S) cycle due to relatively low temperature requirement of 550°C and 900°C respectively. These cycles possess opportunities for efficient integration with other energy systems, in particular, nuclear or solar power. However, the process was complex and required multi-disciplinary approach to develop suitable technology.

In order to accomplish cost effective hydrogen production using thermochemical cycles at commercial scale, the overall development was planned through different stages *viz.* Proof of concept, lab engineering scale, pre-pilot and pilot scale demonstrations leading to commercial production. OEC has been following a collaborative consortium approach in bringing up these technologies on a fast track mode to meet the large hydrogen requirements anticipated in near future in a techno-economically feasible way.

#### **1. Copper-Chlorine (Cu-Cl) Cycle**

OEC in collaboration with Institute of Chemical Technology (ICT), Mumbai has been developing hydrogen production using thermochemical Cu-Cl cycle. The originally proposed cycle by Argonne National Laboratories, USA was modified to the process represented in Fig. 1 consisting six steps. The cycle starts with hydrogen generation (Step-1) where copper and hydrogen chloride gas reacts to produce cuprous chloride (CuCl) and hydrogen. Step-2 is the electrolysis of cuprous chloride to give cupric chloride (CuCl<sub>2</sub>) and copper which is reactant to hydrogen generation reaction followed by drying of aqueous cupric chloride. Further, hydrolysis of CuCl<sub>2</sub> (step-4) produces cupric oxide (CuO) and hydrogen chloride (HCl), a reactant to hydrogen generation reaction and decomposition of CuCl<sub>2</sub> (Step-5) produces cuprous chloride (CuCl) and chlorine gas. The last step is the oxygen generation (Step-6) wherein copper oxide reacts with chlorine to produce cuprous chloride (CuCl) and oxygen. The cuprous chloride from hydrogen generation, decomposition and oxygen generation will be sent to electrolysis.

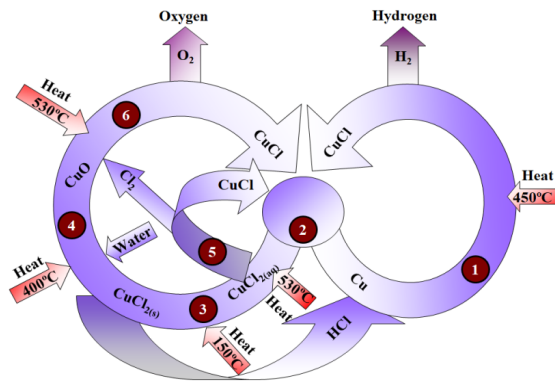
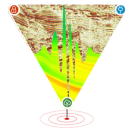


Fig. 1. Closed-loop Cu-Cl thermochemical cycle

Initially, the proof of concept was established in Phase-I by developing a new route for Cu-Cl cycle (patented in seven countries) with no additional energy requirement. All the reactions were experimentally demonstrated with conversions of ~90%. Based on the proof of concept, a metallic set up was developed for 25 LPH H<sub>2</sub> production with indigenous sources. Individual metallic reactors and a series of electrochemical cells/stacks of different capacities were developed and tested for longer durations for performance evaluation. The performance of different anodes, viz. graphite, Platinum (Pt) / MMO coated on titanium was evaluated for electrolysis. Incremental innovations with and novel designs were developed and implemented for process improvement. After satisfied performance of individual reactors, interconnectivity of reactors with one another was established to form the closed loop of Cu-Cl cycle and systems were continuously operated.

In order to address engineering challenges, the facilities for performance evaluation of indigenously developed membranes for electrochemical and gas separation were established and performance of membranes was evaluated. For the development of corrosion resistant materials for plant level operations, the facilities for performance evaluation of different materials in high temperature molten salt media were established. After standardizing the procedure, several metallic and non-metallic materials were screened in molten salt environment at 550°C up to 1000h. After completion of work at each stage, the gaps were identified with respect to challenges.

The performance checks of existing systems for prolonged period, bridge the gap studies to address all the engineering challenges of the Cu-Cl cycle and data generation in progress.

## 2. Iodine-Sulphur (I-S) Cycle (Closed Loop)

RD&D on iodine-sulfur (I-S) thermochemical cycle was initiated by OEC in collaboration with Indian Institute of Technology, Delhi. The reactions in the I-S cycle are shown in Fig. 2. The first one is the Bunsen section, an exothermic reaction, which proceeds spontaneously in the temperature range 298-393K and produces two acids: H<sub>2</sub>SO<sub>4</sub> and HI, however, the other two reactions are the thermal decompositions of those acids formed. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) decomposition is an endothermic reaction, which is composed of two stages, i.e. gaseous H<sub>2</sub>SO<sub>4</sub> decomposes spontaneously into H<sub>2</sub>O and SO<sub>3</sub> at 673-773K and then SO<sub>3</sub> decomposes into SO<sub>2</sub> and O<sub>2</sub> at about 1073-1173 K in the presence of catalyst. HI decomposition is slightly endothermic reaction, releases hydrogen and takes place in the temperature range 573-723K.

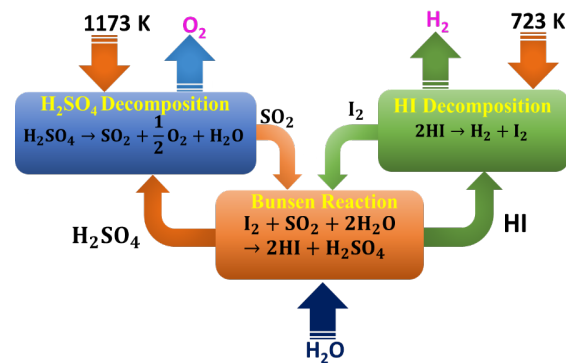


Fig. 2. Closed-loop I-S thermochemical cycle

During the studies, fundamental studies on the three reactions of I-S cycle i.e. Bunsen reaction, HI decomposition reaction, and sulfuric acid decomposition reaction were completed. The issues of separation, concentration and purification sulfuric acid were also addressed.

In H<sub>2</sub>SO<sub>4</sub> decomposition section, a cost-effective, high performing and highly stable non-Pt-based catalyst system was developed and tested. Designed, fabricated pilot scale metallic reactor system equivalent to 150 LPH of H<sub>2</sub> generation in-house.

Performance of selected catalyst under lab stage was evaluated further in this reactor at  $900 \pm 50^\circ\text{C}$  and 10-15 bars and found to be highly satisfactory. Mechanistic studies on catalytic decomposition of  $\text{H}_2\text{SO}_4$  were completed. In HI decomposition section, a highly performing transition metal based catalyst system which is stable for over 100 h was developed and yields conversion being close to equilibrium values at  $500\text{-}550^\circ\text{C}$ .

In Bunsen section, the reaction kinetics and separation characteristics of  $\text{H}_2\text{SO}_4$  and HIx phases were studied through electro-dialysis and electro-electro-dialysis (EED) technique for HI enrichment and established at lab scale with minimum cross-contamination levels across membrane and without any side reactions. Model codes were developed in Simulation work to address scaling up and issues related to integration with the remaining sections of the cycle. In HI section, new catalysts were developed giving near equilibrium conversion and their long-term stability was also tested.

Presently, the data generation from the integrated closed loop I-S process for hydrogen production in all quartz/glass assembly set-up is in progress in view of scale up.

### 3. Iodine-Sulphur (I-S) Cycle (Partially open-loop)

Generally, natural gas processing involves deep removal of hydrogen sulphide ( $\text{H}_2\text{S}$ ), a hazardous pollutant, and post-treating. Presently,  $\text{H}_2\text{S}$  is largely converted to elemental sulfur and water using industrial processes such as the Claus process, however, it would be more useful and economical to convert  $\text{H}_2\text{S}$  to sulfur and  $\text{H}_2$  instead (Spatolisano et al., 2022 and De Crisci et al., 2019).

As large-scale  $\text{H}_2$  production processes from  $\text{H}_2\text{S}$  decomposition have not yet been developed, a low temperature alternate route of thermochemical hydrogen production through partially open-loop I-S process utilising  $\text{H}_2\text{S}$  was explored by OEC in collaboration with CSIR-IIP, Dehradun. This is an offshoot of closed-loop I-S cycle and involves three main steps as shown in Fig. 3 starting from  $\text{H}_2\text{S}$ : (1)  $\text{H}_2\text{S}$  Incineration (2) Bunsen Reaction (3) HI Decomposition. This process does not involve the  $\text{H}_2\text{SO}_4$  decomposition unlike closed-loop I-S cycle. Instead produced  $\text{H}_2\text{SO}_4$  can be marketed to the fertilizer plants. Therefore, this arrangement makes the cycle a partially open loop.

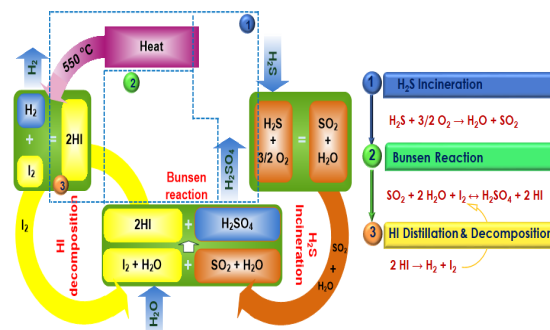
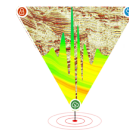


Fig. 3. Partially open-loop I-S thermochemical cycle

The  $\text{H}_2\text{S}$  incineration occurs at temperatures of 1073-1373K in presence of  $\text{O}_2$  to yield  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . This  $\text{SO}_2$  will then reacts exothermically with  $\text{I}_2$  and  $\text{H}_2\text{O}$  in the Bunsen reaction to produce two acids:  $\text{H}_2\text{SO}_4$  and HI. There are two immiscible liquid phases: the  $\text{H}_2\text{SO}_4$  phase, consisting primarily of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ ; and the HIx phase that contains mainly HI,  $\text{I}_2$  and  $\text{H}_2\text{O}$ . The Bunsen reaction is highly exothermic, and for it to spontaneously proceed in the liquid phase, excessive  $\text{H}_2\text{O}$  is required. Another reactant,  $\text{I}_2$ , also needs to be put in excess to separate the mixture of  $\text{H}_2\text{SO}_4$  and HIx phases into two immiscible aqueous phases (a liquid-liquid equilibrium phase separation process). Therefore, purification of  $\text{H}_2\text{SO}_4$  and HIx phases is also required. The next step is the HI decomposition, an endothermic catalytic reaction, releases hydrogen and requires lower temperatures (573-723K).

During the studies, the proof of concept in quartz systems has been established in Phase-I. Although  $\text{H}_2\text{S}$  incineration is a well-established process, to generate process 'know how' to address some critical issues in view of open-loop S-I cycle,  $\text{H}_2\text{S}$  incineration was studied in the laboratory scale  $\text{H}_2\text{S}$  incinerator designed/fabricated based on the simulation and data obtained from Sulphur Recovery Unit (SRU) of the refinery with complete combustion.

During the studies, the Bunsen reaction was optimized to reduce cross-contamination and achieve maximum purification of HIx and  $\text{H}_2\text{SO}_4$  phases. The complete purification of  $\text{H}_2\text{SO}_4$  phase and HIx phases was achieved. In HI section, the catalyst was tested with the HI collected as the distillate after distillation and showed exceptional performance. Presently, the integration of various sub-sections are in progress



now based on which a pilot scale metallic system is planned.

In both the partially open loop and closed loop I-S cycle, the iodine section constituting HI concentration, HI decomposition and H<sub>2</sub> separation from HI decomposition possess significant challenges in terms of complexity and material handling. In order to reduce the temperature requirement of HI section of I-S cycle, feasibility of HI decomposition using electrochemical approach is also being explored.

### **Carbon Recycling Program at ONGC Energy Centre**

Carbon capture and utilization (CCU) is considered an important CO<sub>2</sub> mitigation strategy to support and compliment carbon capture and storage (CCS) objectives for the abatement and sequestration of CO<sub>2</sub>. It represents various pathways that utilize CO<sub>2</sub> as a feedstock in process systems or otherwise for the generation of value-added commodities that should be economically viable and are in high demand.

Under this program, direct heterogeneous catalytic CO<sub>2</sub> hydrogenation to methanol and higher hydrocarbons (HHCs) is being explored.

Highly selective and stable heterogeneous catalysts and supports were synthesized for CO<sub>2</sub> hydrogenation to methanol synthesis. The process parameters, such as temperature, pressure, WHSV, CO<sub>2</sub>/H<sub>2</sub> ratio on CO<sub>2</sub> conversion and product selectivity were optimized and the proof of concept for CO<sub>2</sub> hydrogenation to methanol has been established. Moreover, novel catalyst-support systems for CO<sub>2</sub> hydrogenation into higher hydrocarbons are under development.

### **Indigenous efforts of OEC in entire Ecosystem of Hydrogen generation**

Despite challenges in indigenous development of such technologies for the first time in India that are even yet to be commercialized elsewhere in the world, OEC has made significant strides in the development of these processes, including the supporting technology like membranes, catalysts, electrodes, design of corrosion test methods for screening / materials of construction, indigenous sources of fabrication, etc., and earned several

national and international patents for the developed products and processes.

OEC has established the processes *viz.* close-loop Cu-Cl cycle and close/open loop I-S cycle so far at lab / lab engineering scale and is in the process of scaling up at ONGC premises for process intensification using in-house designs and indigenous fabrications in an effort to move forward for realizing ultimate commercialization goals.

Overall, efforts are being made by OEC for cost effective green hydrogen ecosystem on a fast track mode to meet the large hydrogen requirements anticipated in near future in a techno-economically feasible way.

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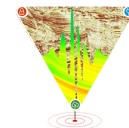
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