Developments in thermochemical Hydrogen Production processes at BARC

Dr A Shriniwas Rao
Chemical Technology Division
Bhabha Atomic Research Centre
Mumbai, India

Outline

- Introduction
- Iodine Sulfur Process
  - Glass closed loop
  - Metallic closed loop
- Hybrid Sulfur process
  - Glass closed loop
  - Metallic closed loop
- Variants of S based processes
- Copper Chlorine Process

Introduction

- Energy demand
- Fossil fuels
- Green house gas emissions
- One potential opportunity
  - To replace the use of fossil fuels by hydrogen (by clean energy sources such as nuclear, solar, wind, hydro or high grade industrial heat)
- Hydrogen is
  - Clean
  - Abundant
  - Convenient to use
  - Independence from foreign control

Iodine Sulfur process

Advantages of Iodine-sulfur (I-S) Process

- High predicted thermal efficiency of around 50%
- Closed loop process - All chemicals are recycled within system
- All fluid process
- It's capability to be coupled to
  - ✓ A high temperature nuclear reactor (HTR)
  - ✓ Solar concentrated heat
  - ✓ High grade industrial heat
- Promising method for
  - efficient
  - green house gas emission free
  - large scale hydrogen production

Iodine-Sulfur Process

1.Bunsen Section

A. Bunsen Reaction

B. Liquid-Liquid Separation

C. Acid Purification

2. HI section

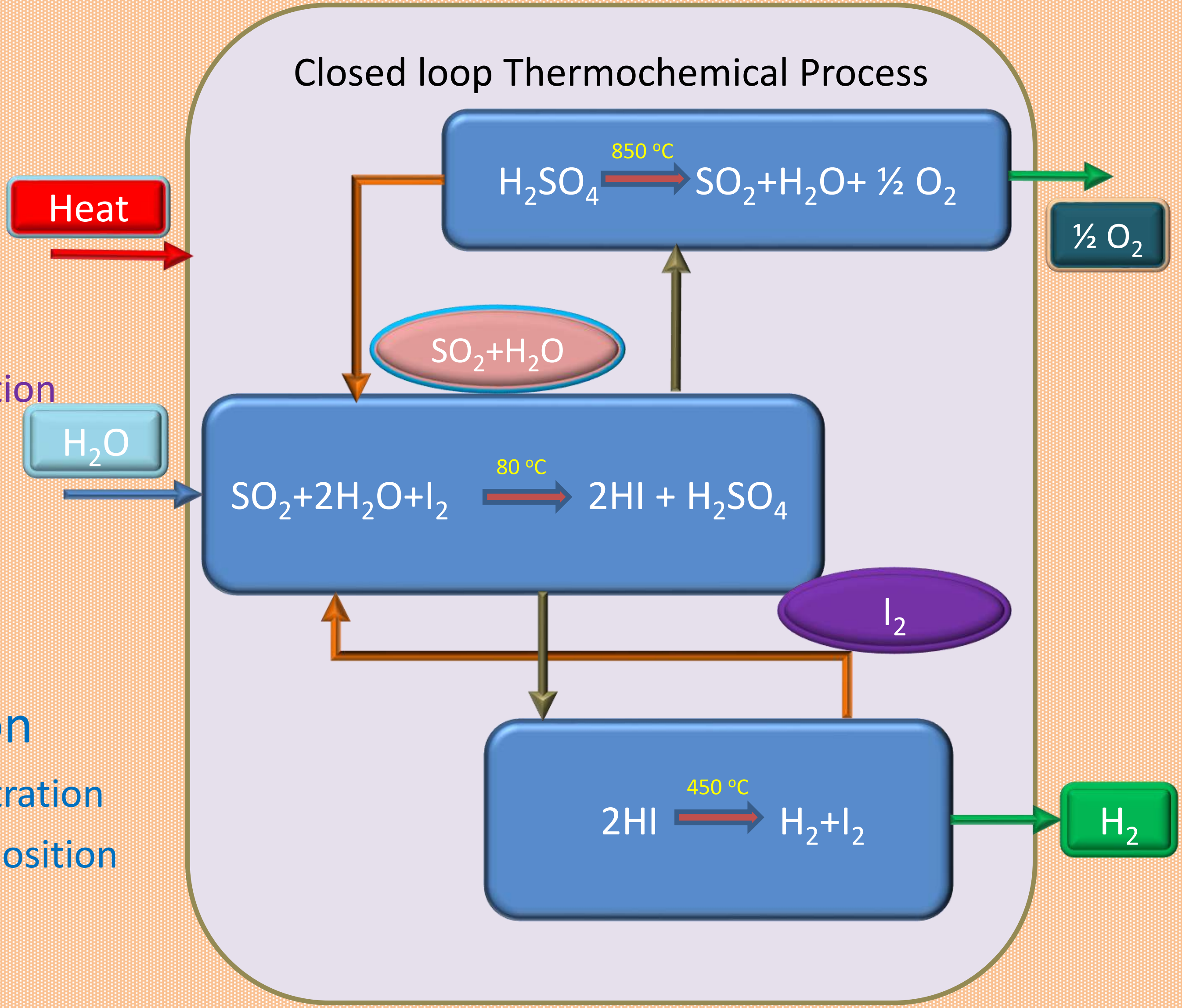
A. HIx distillation

B. HI decomposition

3. Sulfuric Acid Section

A. Sulfuric acid Concentration

B. Sulfuric acid Decomposition



Overall reaction: 

I-S PROCESS : Options in each section

BUNSEN SECTION

- Flow Reactor
- Electro Chemical Membrane Reactor

HI SECTION

- Reactive Distillation Column
- Electro-electro Dialysis
  - Distillation
  - Membrane Reactor For HI Decomposition
- Coupled Membrane & Reactive Distillation

Sulfuric Acid (SA) SECTION

- Isobaric Concentration
- Membrane Reactor
- Direct Contact Method

Objective of I-S process in glass setup

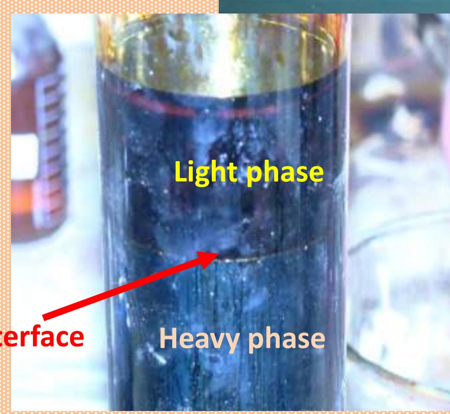
- To study the feasibility of operation
- To study stability/controllability of operation
- To use the catalysts developed for HI and SO_3 decomposition in closed loop conditions
- Testing of equipments, pumps and monitors

Closed Loop Glass setup

Liquid-liquid separator

Sulfuric acid purifier

HIx purifier



Interface

Bunsen reactor

HI Distillation column and HI decomposer

HI recovery column

Sulfuric acid concentrator and decomposer

Sulfuric acid decomposer operating at 900 º C.

Sulfuric acid distillation

Distillation column

I-S Process Demonstration in Glass setup

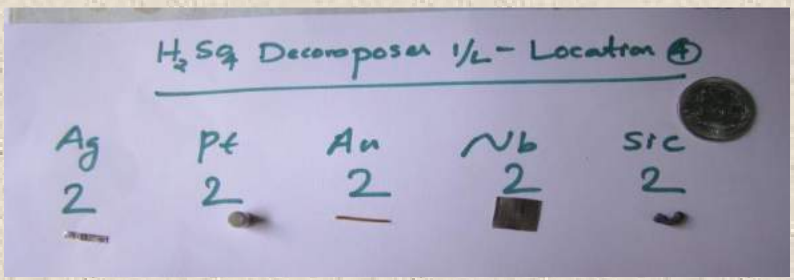
- Studied the process in glass/quartz equipments
- Input - Only water and heat
- Output - H_2 and O_2
- Recycled - SO_2, Iodine, H_2O

- All three sections were operated – simultaneously
- Operated continuously to produce Hydrogen at 30 Nlph
- The feasibility of closed loop operation - established
- India is the 5th Country to achieve this

Work carried out for Industrial I-S process

Identification of compatible MoC

- Corrosion test study has been done with special metals, ceramics, polymers such as <u>Tantalum, Hastelloy, Incoloy, SiC, PTFE and noble metals</u>

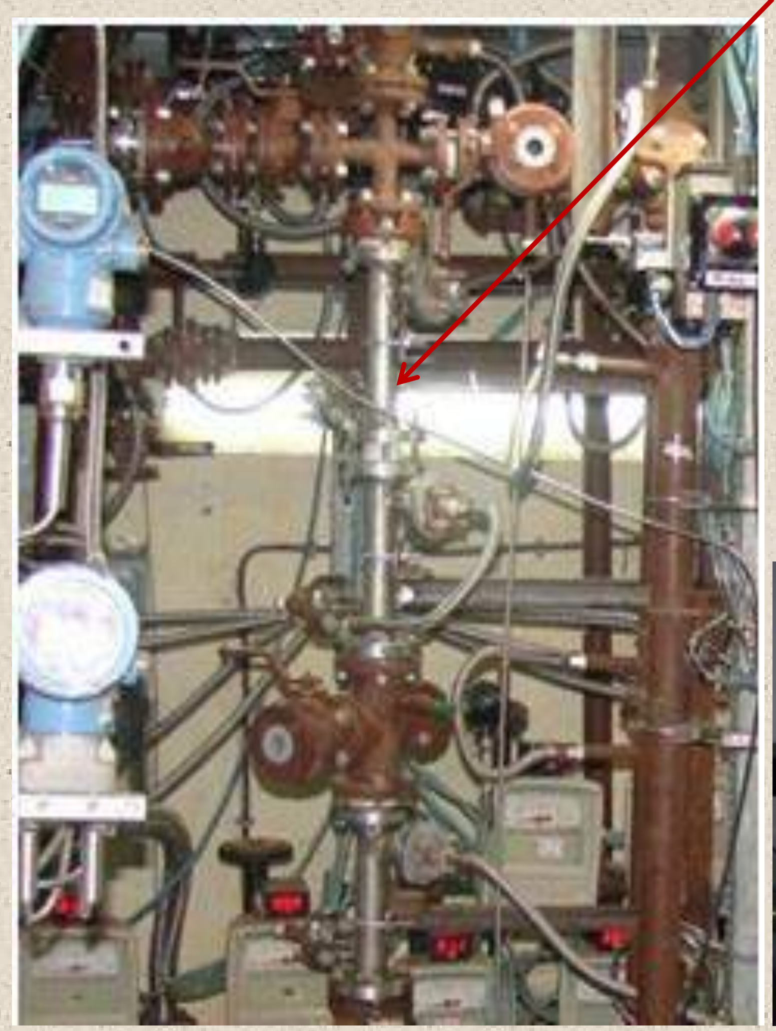


Typical coupons exposed in the test setups

Equipment	Operating Temp (^oC)
H_2SO_4 Decomposer	~500°C
SO_3 Decomposer	~900°C
HI Decomposer	~500°C
H_2SO_4 Boiling/Vaporisation	~337°C
HI Boiling/Vaporisation	~127°C
HIxD Reboiler	~180°C
HIx distillation column	~127-180°C
Sulfuric acid distillation column	~120-270°C

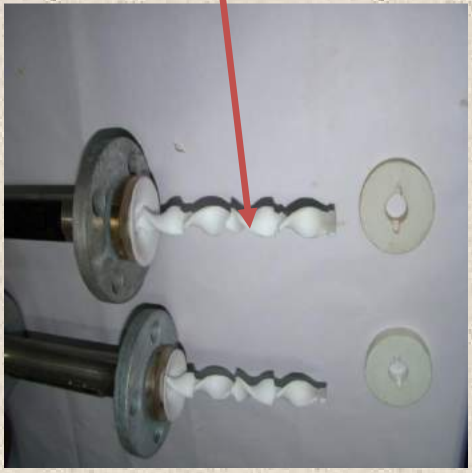
High pressure Bunsen Reaction Setup

Bunsen Reactor



- The Bunsen reactor is a tubular reactor
- The reactor is made of tantalum tube with SS 316 jacket.

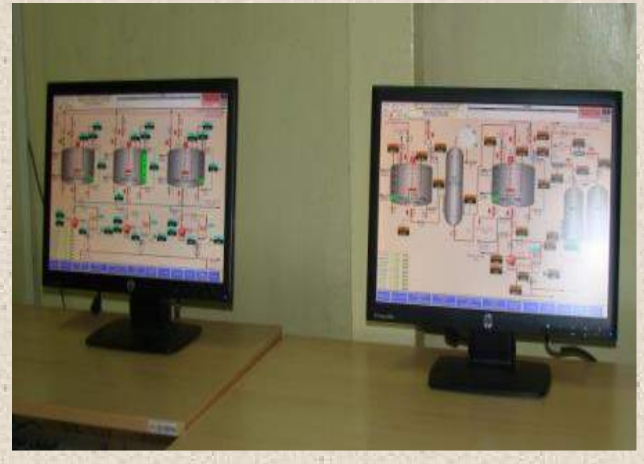
Static Mixer elements



Tantalum Tube

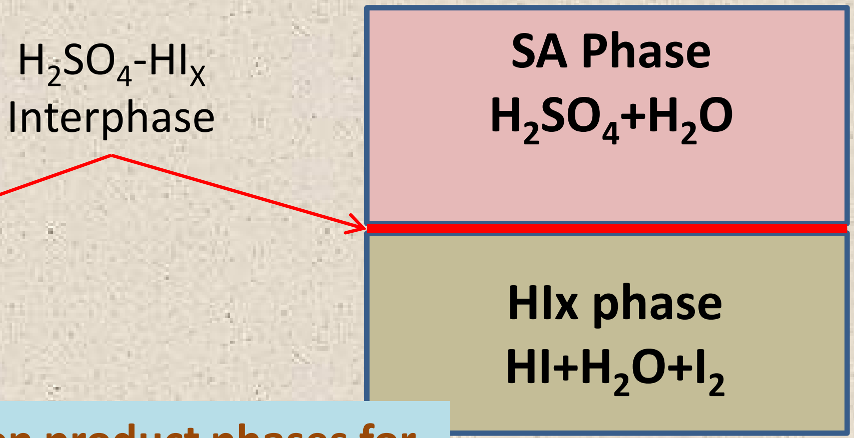
Feed tank and operating console

Iodine Feed tank



Operating parameter range

Parameter	Ranges
Operating temperature	60 °C to 80 °C
Operating pressures	2 bar (g) - 6 bar (g)
Flow rates of feed HIx	1.2 l/h to 3 l/h
I_2/ H_2O mole ratios	0.22-0.36
Feed flow rate of SO_2	0.02 g/s – 0.24 g/s

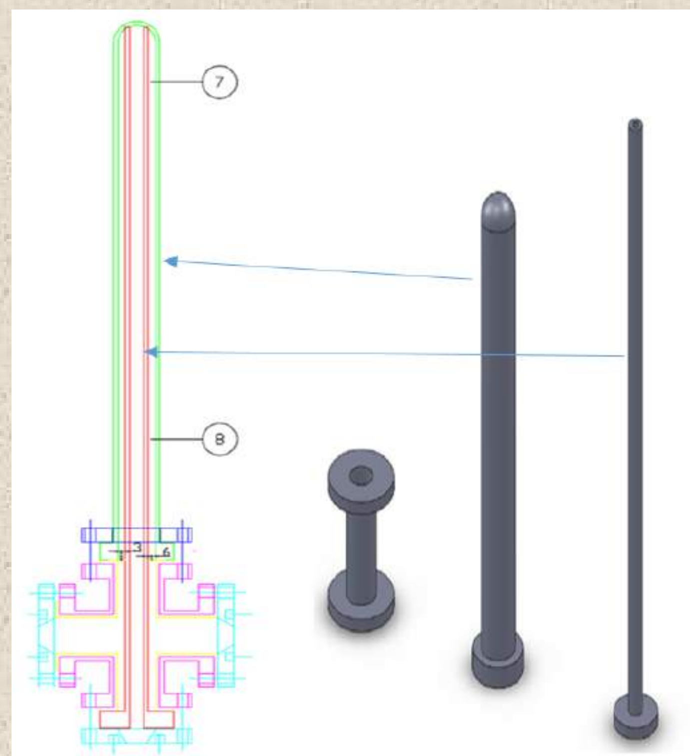


Bunsen reaction product phases for experiment at 6 bar (g) and 70 °C

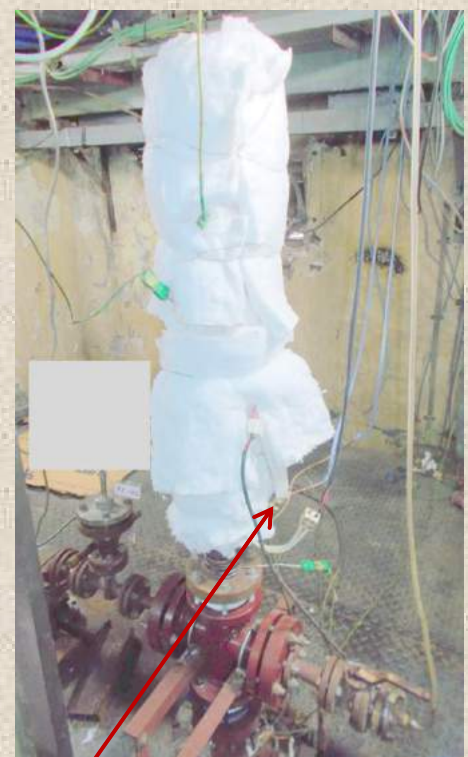
High pressure Bunsen Section- Remarks

- Feasible to carryout in continuous mode
- The desirable operating range identified
- Know how of design & operation procedures established
- *Knowledge & experience utilized for 'Metallic Closed loop'*

Components for Sulfuric acid decomposition

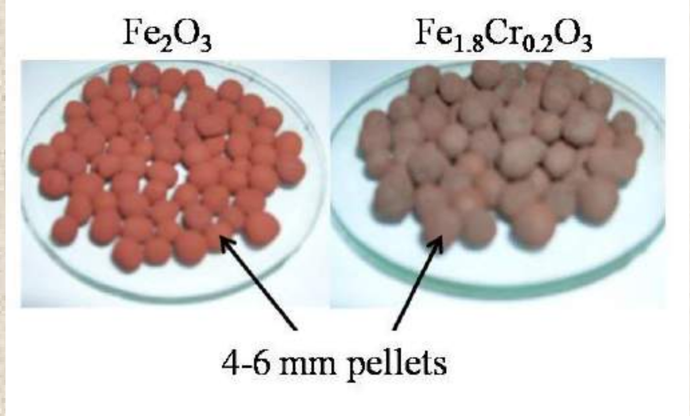


SiC- Bayonet tube reactor



SiC reactor developed, tested at 900 °C for H_2SO_4 vaporisation and decomposition

Catalyst for Sulfuric Acid Decomposition



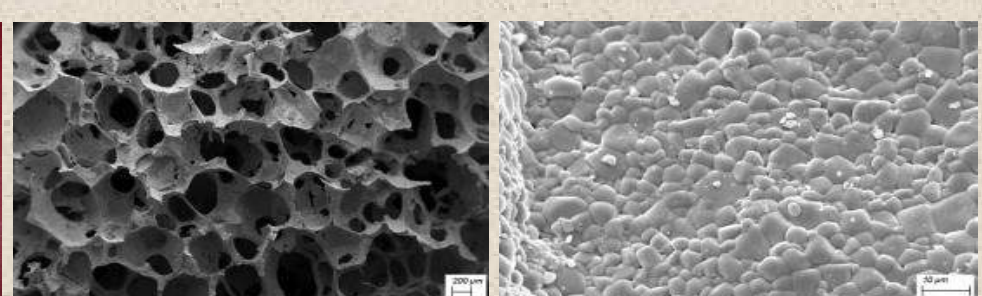
- Cr-doped Fe_2O_3 - developed non-noble catalyst
- Cr-doping improved - activity & stability
- Mechanism understood - Formation & decomposition of transient metal sulfate

Development of *Ceramic Foam* type Catalyst for Sulphuric acid decomposition

- Ceramic shaping techniques used - to address issues of pore stability & degradation with time
- Template Foam - impregnated with ceramic slurry later sintered
- Catalyst exhibited high performance
  - >80% up to 100 h in laboratory conditions
  - Larger batch exhibited ~72% yield in reactor
  - Stability with time

Template Foam

Iron Oxide foam



SEM image showing pores & strut in iron oxide foam catalyst

HI decomposition

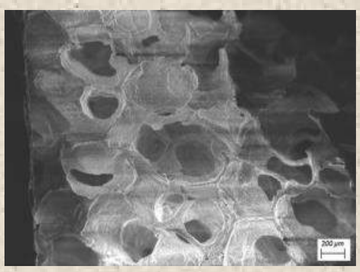
- Membrane tube developed - to separate hydrogen from Iodine, HI and H_2O at high temperature
- Single tube membrane reactor setup is installed and tested
- Multi tube membrane reactor tested
- Achieved more than 80% one pass conversion of HI against equilibrium conversion of ~ 22 %.

Development of *Ceramic Foam* type Catalyst for HI decomposition

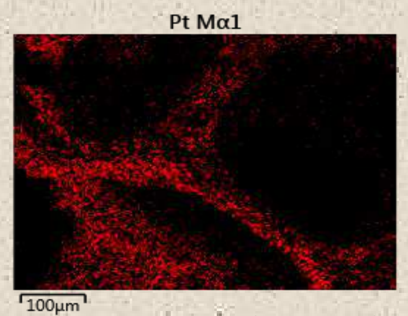
- Pt-loaded gamma-alumina catalyst developed
- Ceramic foam type catalyst prepared by
  - impregnating template foam with alpha-alumina slurry
  - followed by sintering & coating with gamma alumina slurry
  - support ceramic foam coated with platinum
- The catalyst showed uniformity in structure and good performance (~20% equilibrium yield)

Alumina foam

After introducing platinum



SEM showing pores



EDS showing uniformity of Pt

Demonstration of I-S Process in MCL

Objectives of the project:

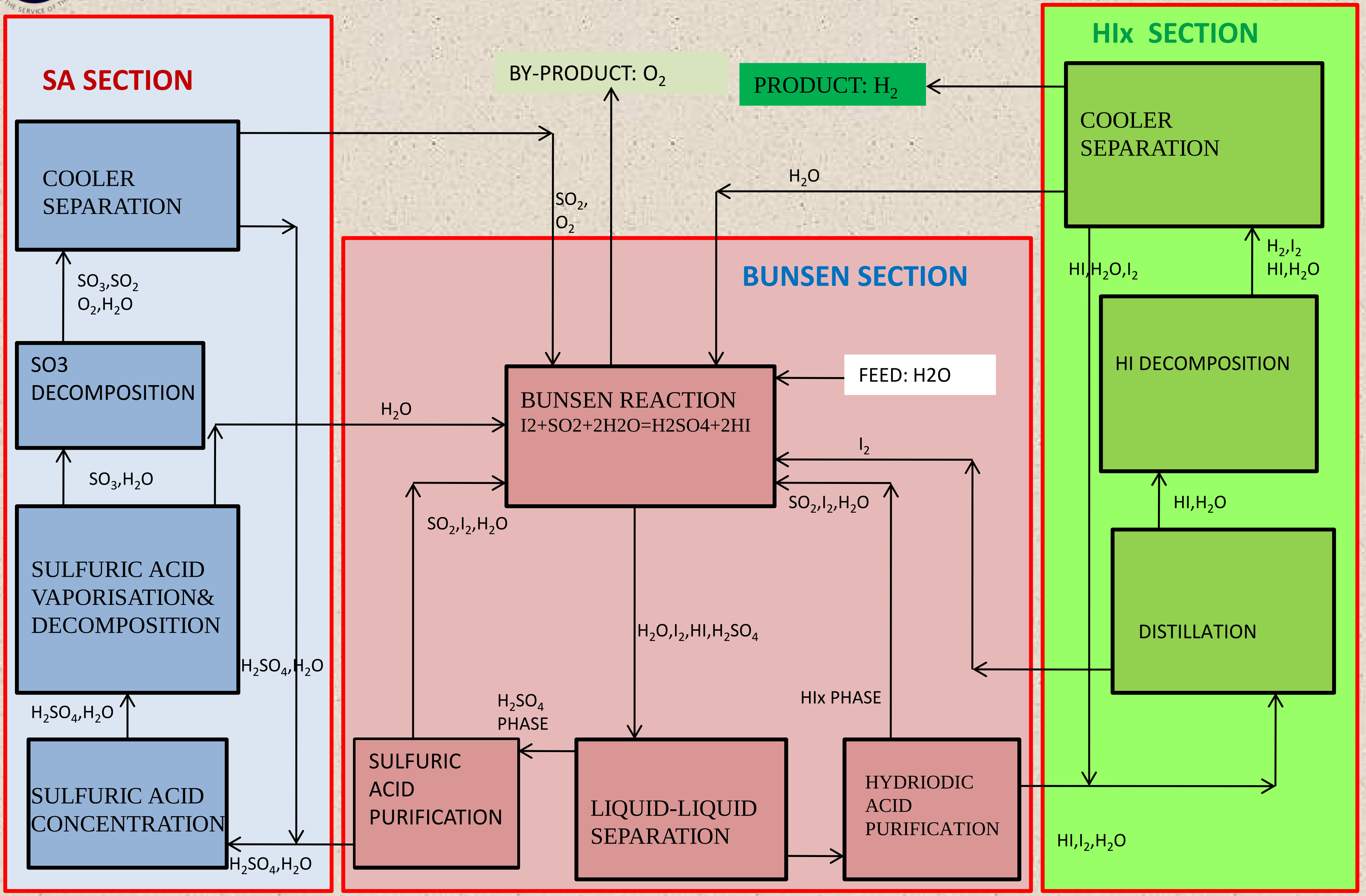
✓Demonstration of I-S process in metallic closed loop (MCL)

- Nominal Capacity : ~ 150 Nlph of hydrogen
- Heating : Electrical energy

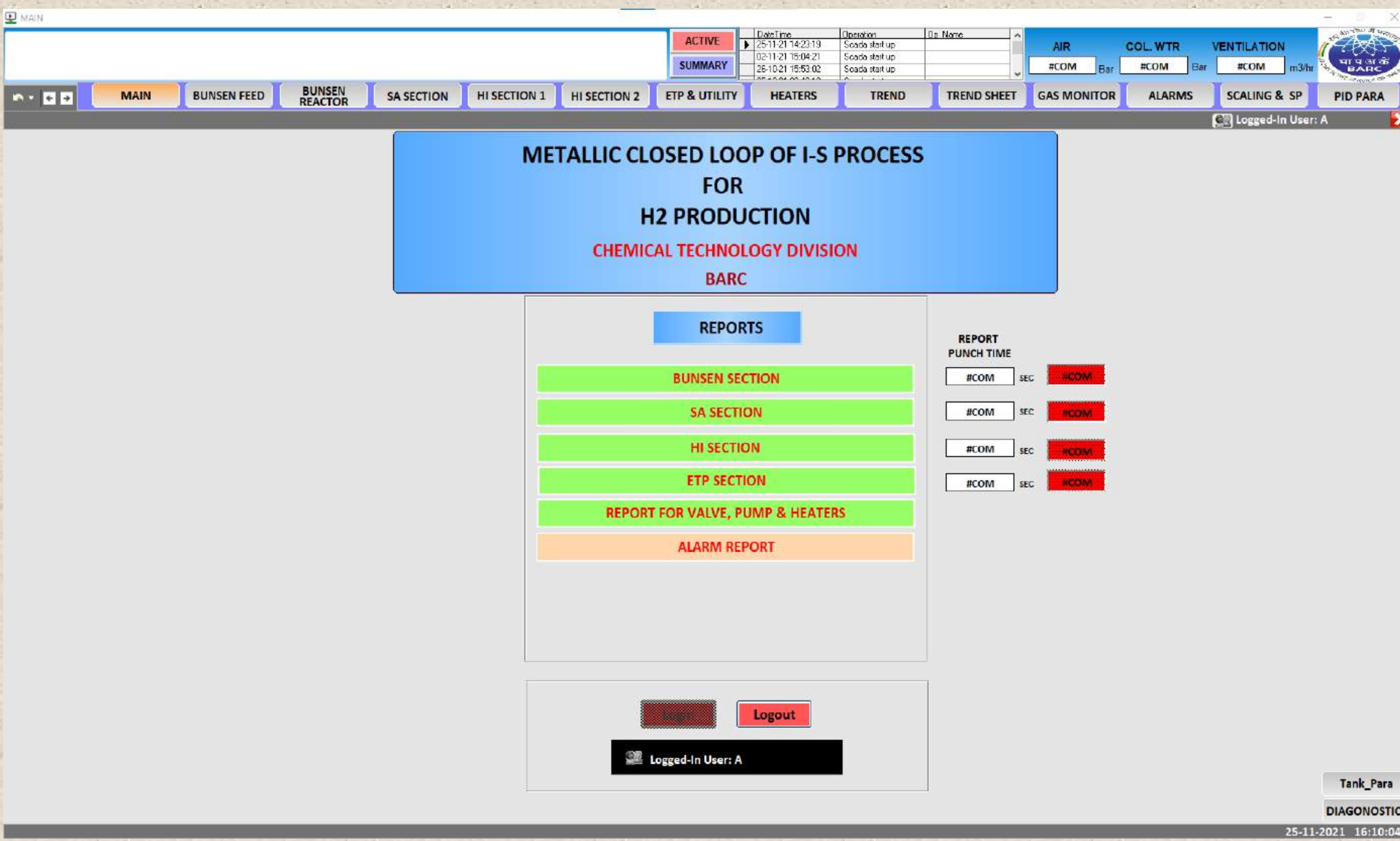
Expected Deliverables / Outcome of MCL:

1. Operating experience of the closed loop facility with recycling of chemicals
2. Standardization of measurement & control techniques
3. Study of engineering scale materials under closed loop condition

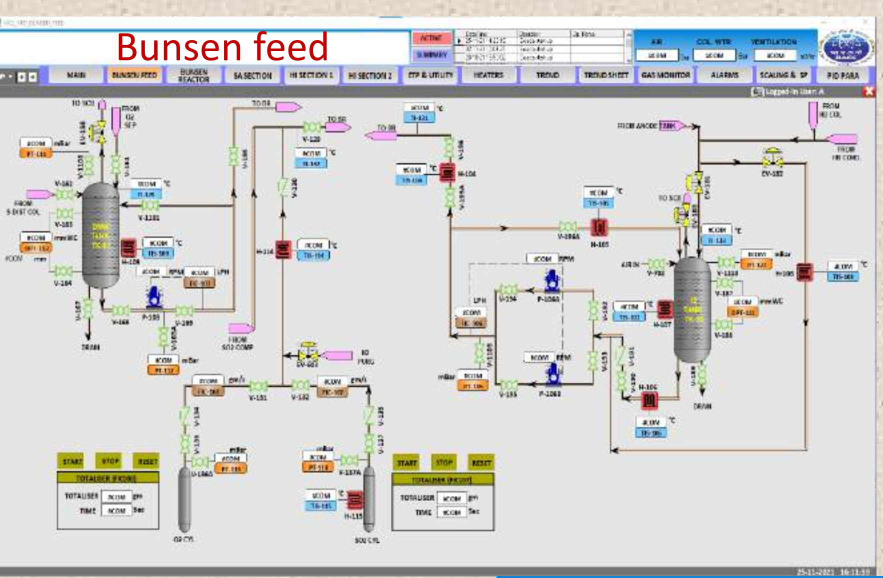
I-S PROCESS BLOCK DIAGRAM

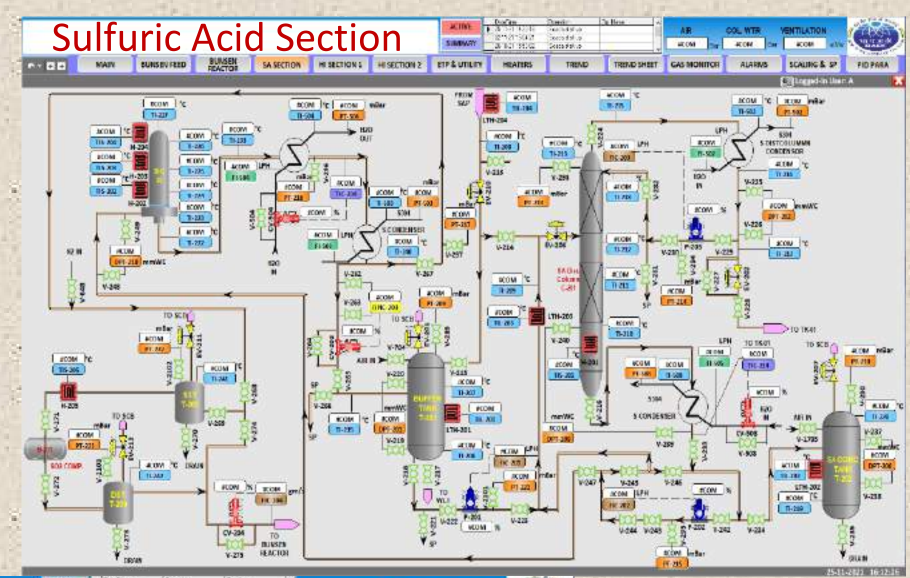


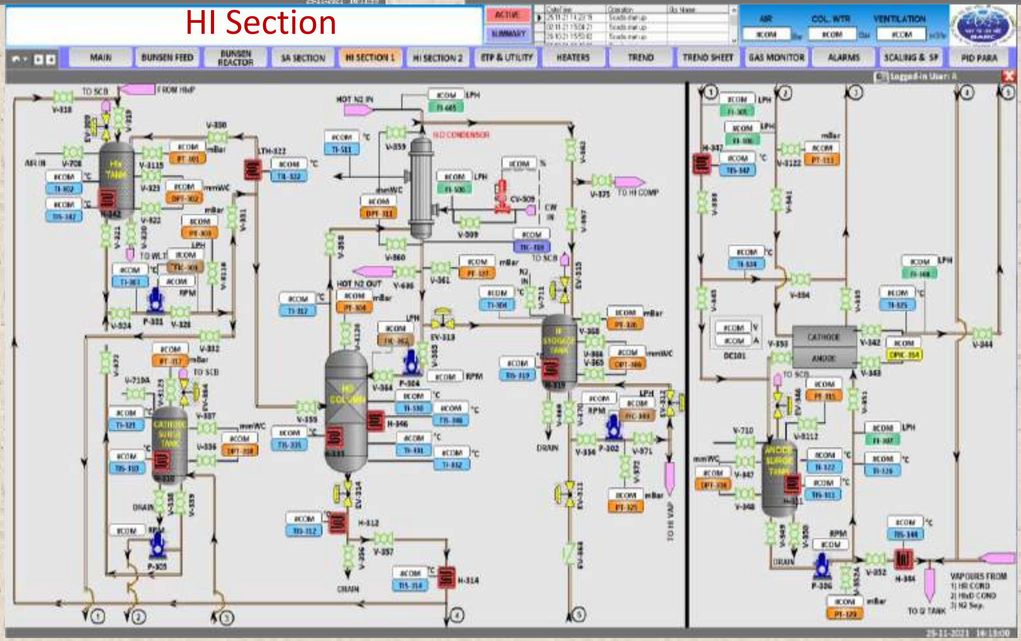
Main SCADA Screen of I-S Process



Mimic Screes in SCADA system

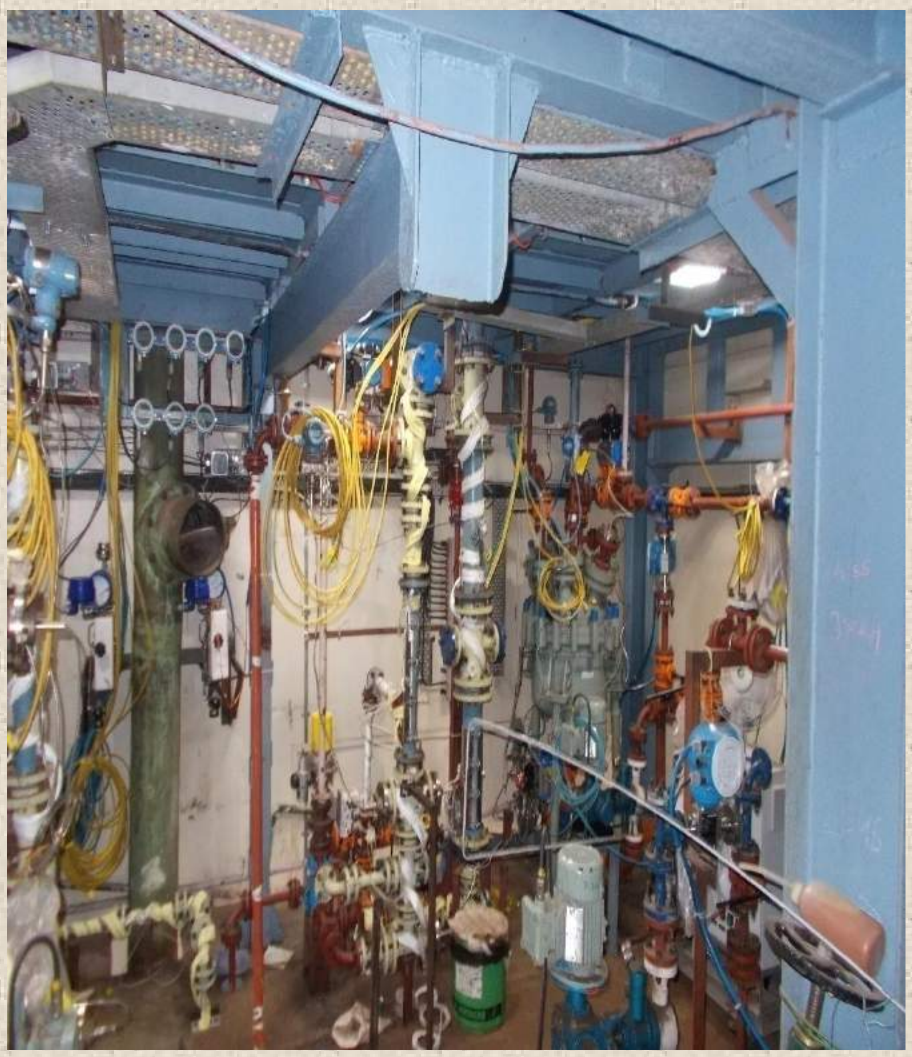






Bunsen Section of I-S Process facility

First floor of I-S Process facility



Second floor of I-S Process facility

Achievements of I-S Process MCL

- Counter-Current Bunsen reaction cum phase separation - achieved for the first time.
- HIx distillation - successfully carried out for the first time.
- Complete purification of SA phase - achieved.
- Commissioned - Bunsen reactor, HI decomposer, SA decomposer, Concentrators and purifiers.
- Studied individual equipment initially, then individual sections (Bunsen section, HI section, SA section)
- Combined all the three sections - to close the loop
- Hydrogen is produced at 150 Nlph
- ‘First of its kind’ with industrial materials & all plant features

Hybrid Sulfur process

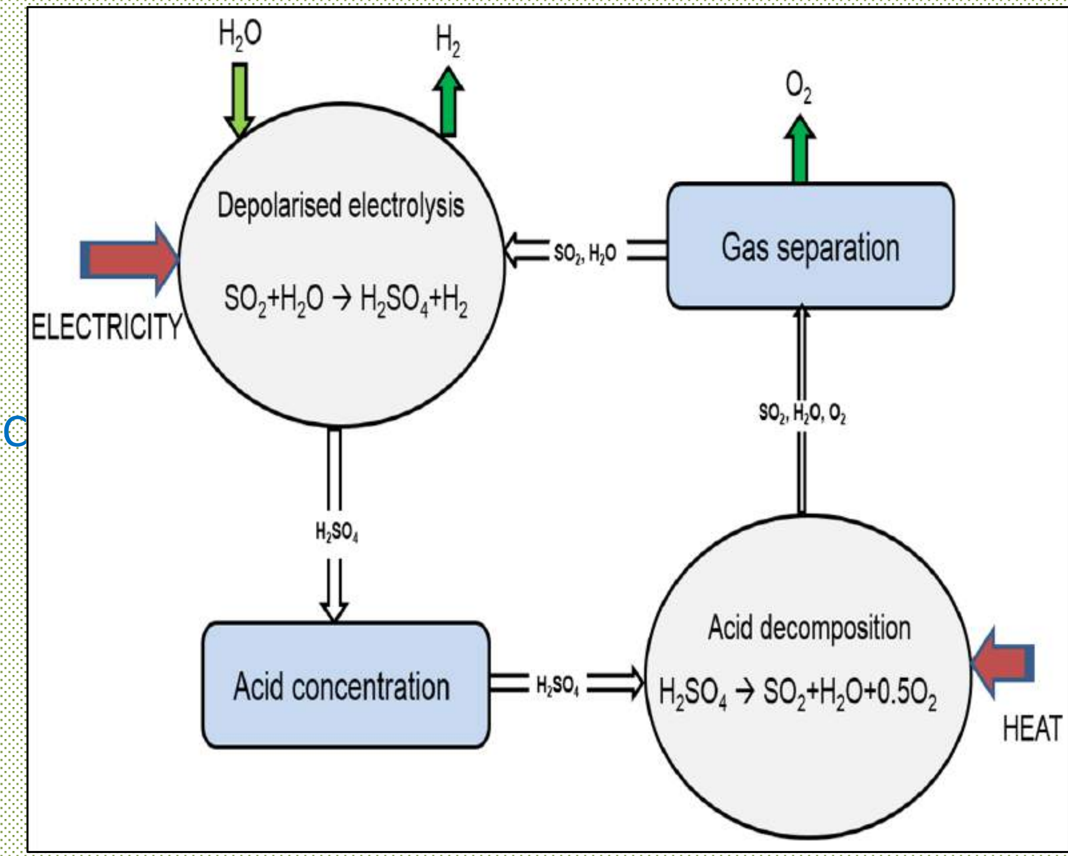
Hybrid-Sulphur (HyS) water splitting process

2 steps/reactions

1. H_2SO_4 & H_2 generation step
   (Electro-chemical step, ~80°C)

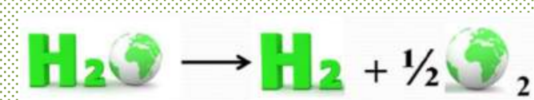
2. H_2SO_4 decomposition step
   (Endothermic-catalytic reaction, ~850 °C

- Hybrid process: Require both heat & electricity
- *Thermal efficiency ~45%*



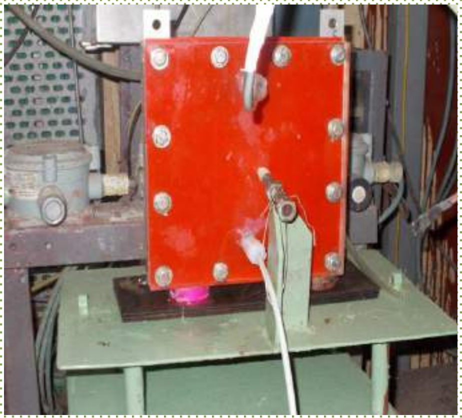
HyS process schematic

Overall reaction:

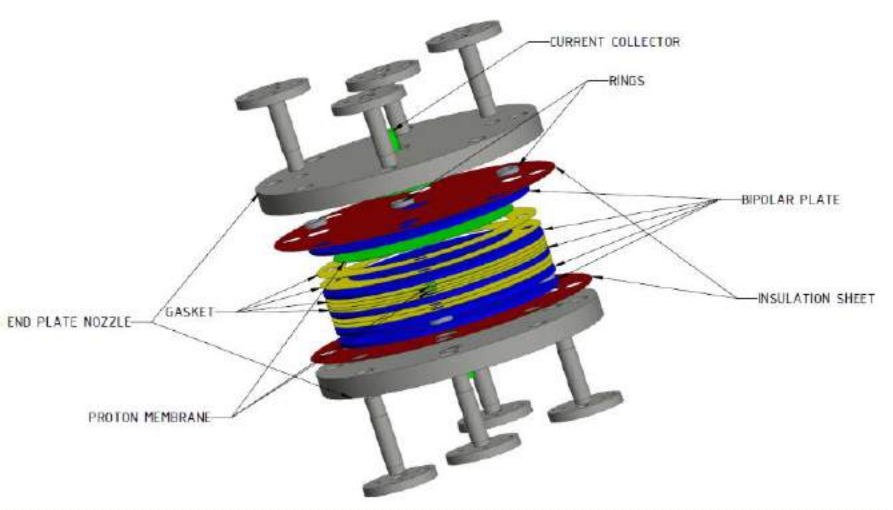


SO_2 depolarised electrolyser (SDE)

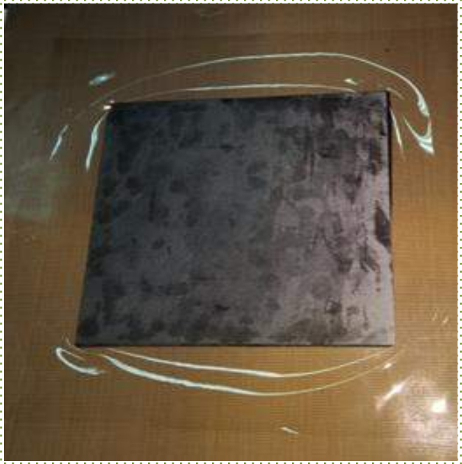
- **$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$**
  - reaction in SDE
- Single cell SDE (16cm×16cm) is fabricated and tested
- Membrane electrode assembly (MEA) is prepared and tested
- Stacked SDE is fabricated & assembled



Single cell SDE



Stacked SDE sized & fabricated

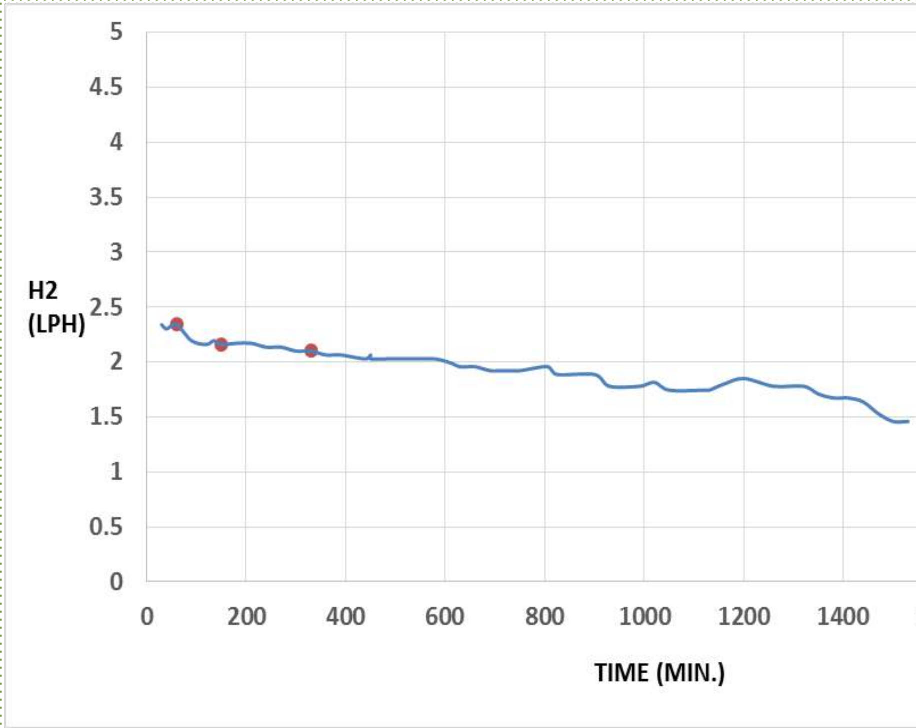


MEA

HyS demonstration

- Objective: To establish the feasibility of process for continuous operation in lab scale (glass/quartz set up)

- Closed loop operation has been carried out successfully
  - H2 production at a rate of ~2 Nlph
  - Input: H_2O & electricity, Output: H_2 & O_2 , intermediate chemicals- recycled



H_2 Production rate

HyS Experimental Facility - MCL

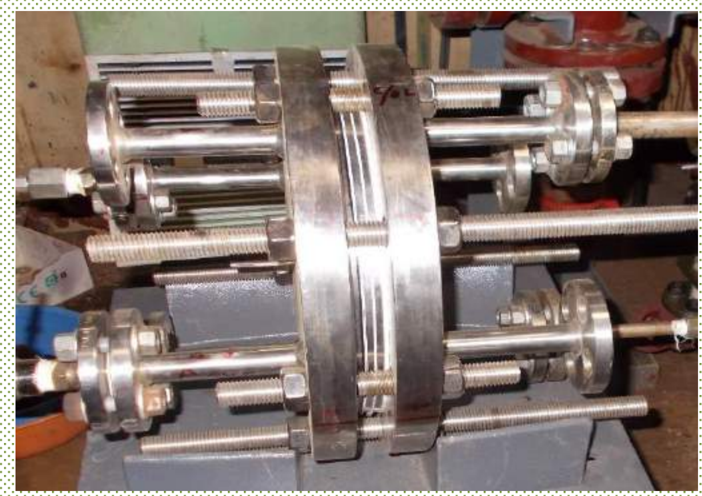
Objective:

- Demonstration of continuous operation using industrial MOC
- ✓ Electrically heated facility
- ✓ High pressure operation

<u>H_2 production at a rate of 10 Nlph is achieved</u>

HSEF: tanks and piping

'SiC' reactor



2 cell stacked electrolyser (SDE)

H_2 & H_2SO_4 from variants of Sulphur based process

Variants of IS & HyS processes

- I-S and HyS process can be altered to utilize the H_2S, SO_2 produced in the Refineries, Zn & Cu industries to produce H_2

Refinery Industries

Heat & H_2S, SO_2

Zinc Industries

Heat & SO_2

Copper Industries

Heat & SO_2

$H_2S + I_2 \rightarrow 2\ HI + S$

$2\ HI \rightarrow H_2 + I_2$

H_2, S

$2\ H_2O$

$SO_2 + I_2 + 2\ H_2O \rightarrow H_2SO_4 + 2\ HI$

$2\ HI \rightarrow H_2 + I_2$

H_2, H_2SO_4

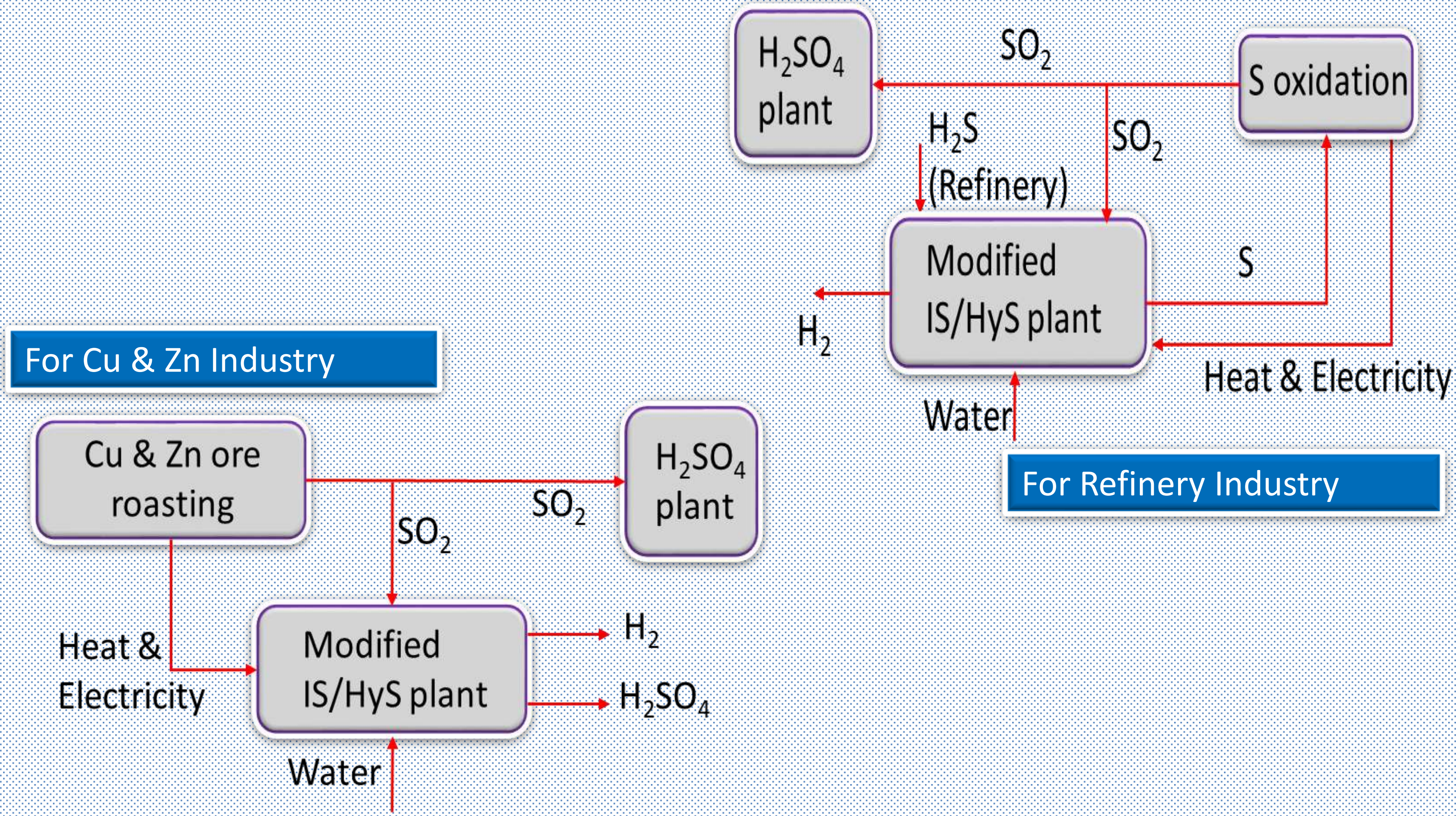
Modified I-S Process

$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + H_2$

$2\ H_2O$

SO2 Depolarized Electrolyzer, (Modified HyS)

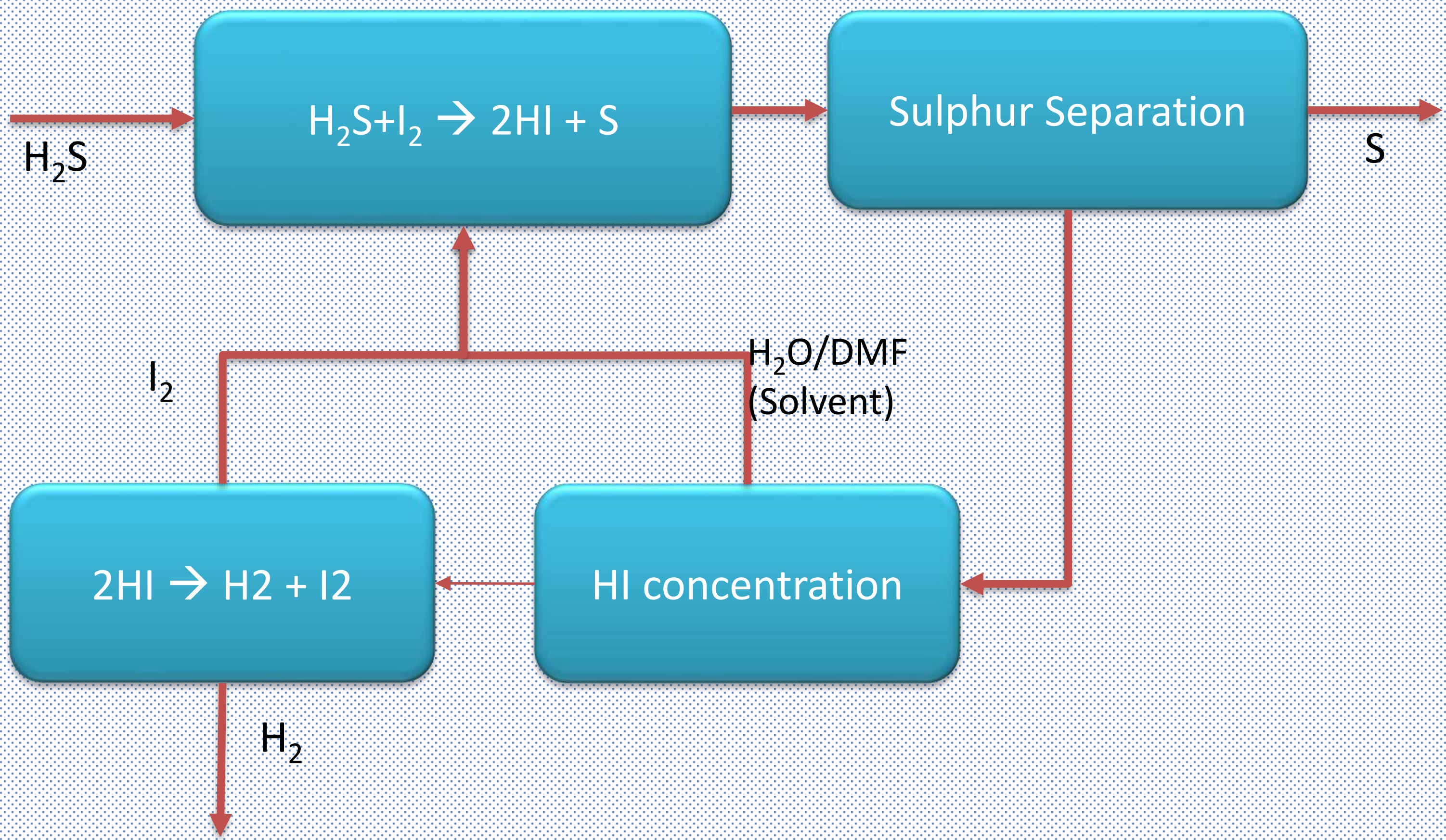
Schemes for H_2 production from H_2S and SO_2



Advantages of modified IS & HyS processes

- More efficient utilization of exothermic heat of Sulphur/ZnS/CuS reactions
  – to carry out decomposition of HI (450°C)
  – in reboiler of HI distillation column (250°C)
  – in Sulphuric acid and HI purifier (150°C)
- Better utilization of CPP power to drive electrochemical step of HyS process & produce H_2
- Avoiding high temperature (850°C), Sulphuric acid decomposition step

Block Diagram for closed loop H_2S to H_2 process



Feasibility Studies

- Water as solvent
  - ✓ Carried out reaction experiments of H_2S and I_2
  - ✓ Products obtained are HI and S
  - ✓ Reaction is feasible
  - ✓ Separation of solid S is done
  - ❑ HIx section
  - ✓ Distillation of HI, I_2 and water
  - ✓ HI decomposition
  - ✓ Hydrogen production

BARC's technological know-how of HIx section viz HIx distillation, HI decomposition, I_2 recycle and related systems for Hydrogen production are readily available

Feasibility Studies

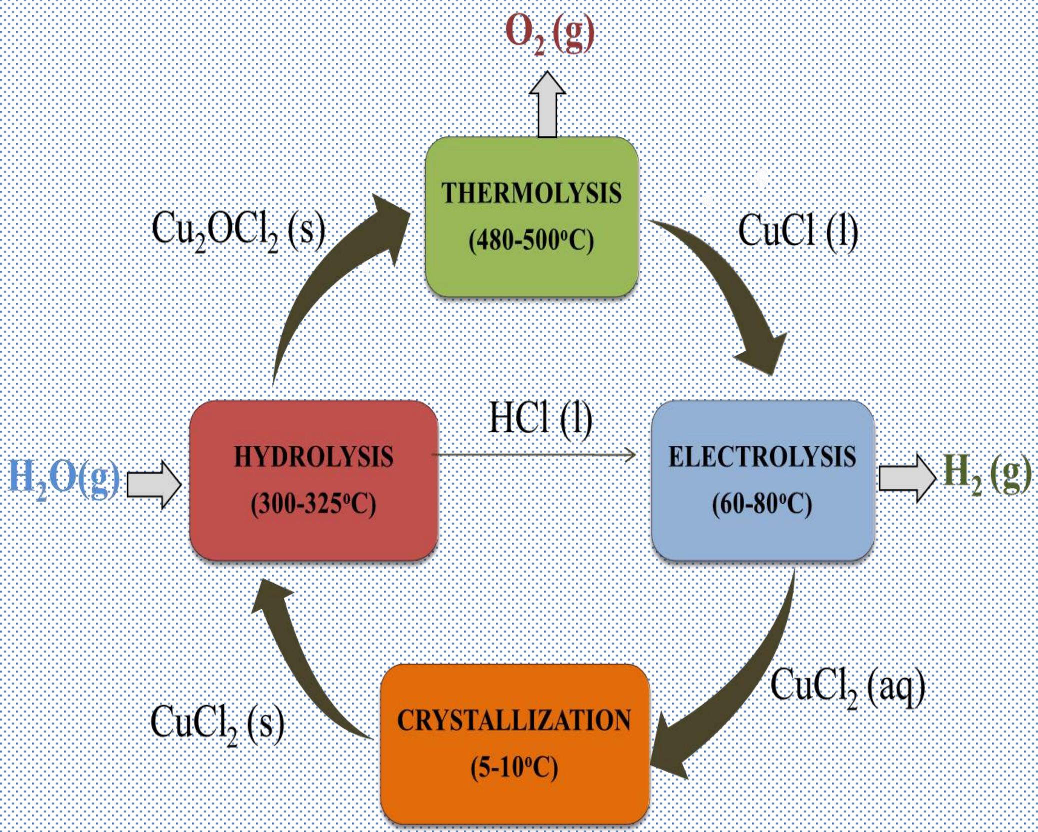
- DMF (Dimethyl formamide) / DMA (Dimethylacetamide) as solvent
  - ✓ Carried out reaction experiments of H_2S and I_2
  - ✓ Products obtained are HI and S
  - ✓ Reaction is feasible

More studies are required wrt reaction and then followed by distillation

After S separation, BARC's technological know-how of HIx section is readily available, for Hydrogen production

Copper-Chlorine process

Four step Copper-Chlorine process



- Hybrid cycle
- Typical efficiency ~ 45 %
- Maximum temperature ~ 500°C

Advantages

- Lower temperature
- Integration with
  - Molten Salt Breeder Reactor
  - High Temperature Reactor
  - Solar heat source

Overall reaction:

Cu-Cl cycle Facility

Achievements Cu-Cl process

TRL – 5

- ✓ Corrosion studies performed - MoC selected
- ✓ Bench scale integrated process - demonstrated
- ✓ Inhouse MEA developed for CuCl-HCl Electrolyzer
- ✓ Energy efficient auxiliary sub-systems developed
- ✓ Hydrogen production of 5 Nlph - achieved
- ❑ Design of 150 NL/h hydrogen plant in advanced stage

Immediate future …

Today – Electrolyser

Tomorrow's technology for large scale Hydrogen plants

- IS and HyS process is developed with indigenous components – participation of PSUs, Industry for higher scale plants
- Variants of IS and HyS to recover hydrogen from H_2S and use high grade industry heat
- Cu-Cl process has advantage of temperature

धन्यवाद

Jai Hind