

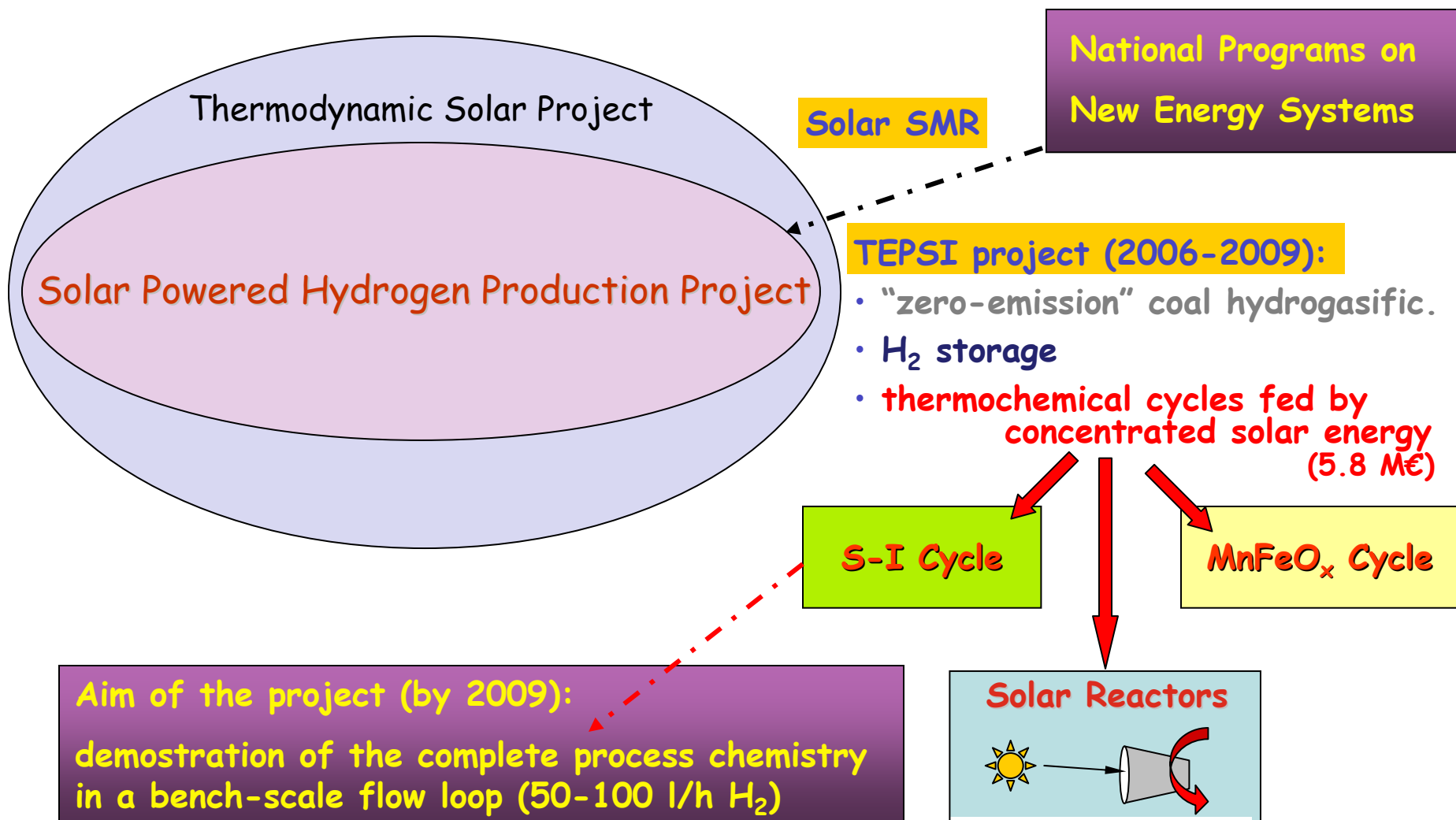
Continuous Flow Operation of a Bunsen Reactor in the Iodine-Sulfur Thermochemical Water-Splitting Cycle

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Outline

- ✓ Research context (brief overview)
- ✓ Previous work done on the Bunsen reaction
- ✓ Arrangement and operation of a continuous Bunsen reactor
- ✓ Use of metallic sulfates in the H_2SO_4 decomposition section
- ✓ Conclusions and future work



Research Context

TEPSI Project (2006-2009) *scientific feasibility demonstration*

targets

→ **Production at laboratory scale** **0.001 ÷ 0.01 m³ / h**

→ **Bench production** **0.05 ÷ 0.1 m³ / h**

(demonstration of the complete process chemistry in an integrated laboratory scale flow loop)

future (2009-)

technological feasibility demonstration

Pre pilot production **30 ÷ 90 m³ / h**

(Design, fabrication and operation of an engineering demonstration loop)

Pilot production **400 ÷ 800 m³ / h**

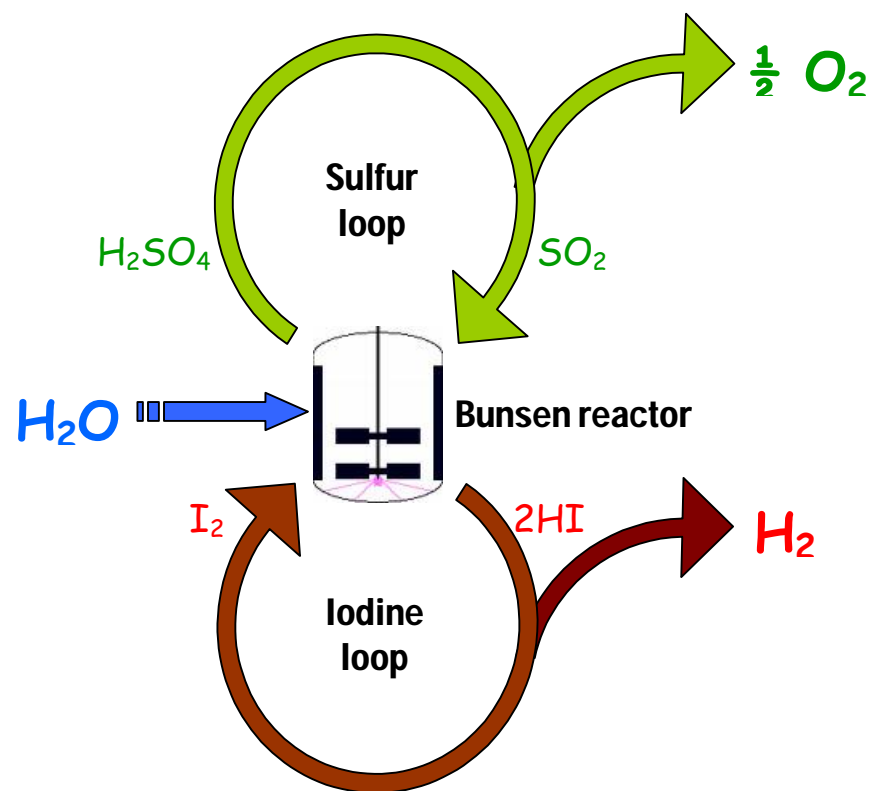
(Design, fabrication and operation of a small hydrogen production demonstration plant)

Objective: Realization of a continuous Bunsen reactor



General objectives:

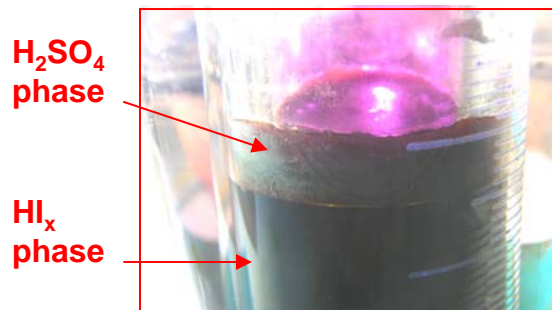
1. Continuous flow operation of the Bunsen reactor must be achieved for closed loop demonstration
2. Operative parameters studied for cycle performance improvements: production of acid streams as pure and concentrated as possible
3. Side reactions to be avoided
4. Basic data for large scale design



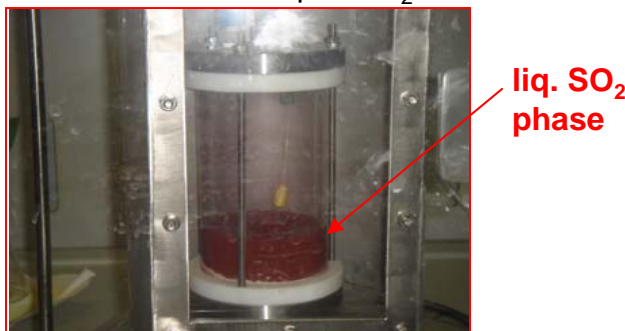
Bunsen reaction options



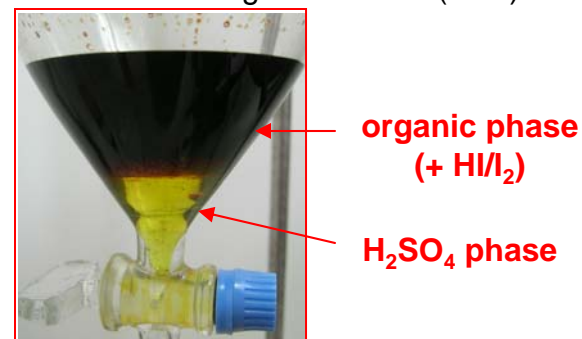
Bunsen in water media



Bunsen in liquid SO₂

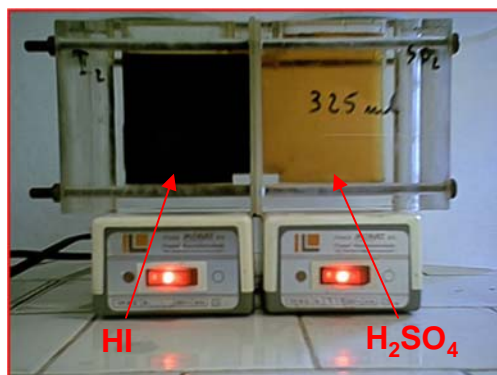


Bunsen in an organic solvent (TBP)



De Beni G. *et al.* Int. J. Hydrogen Energy (1980)

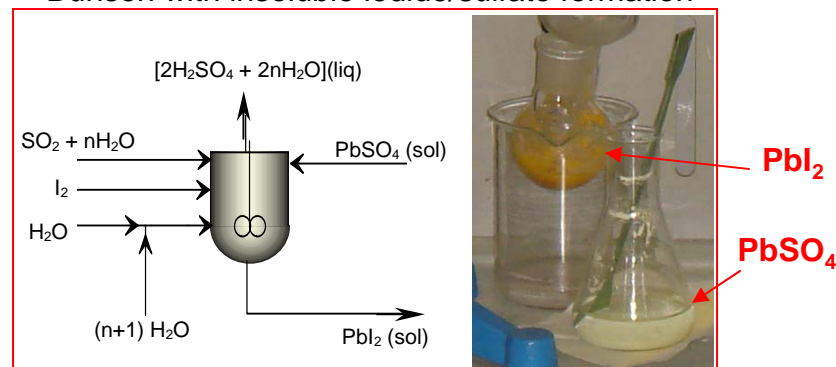
Electrochemical Bunsen



Nomura M. *et al.* J. Membr. Sci. (2004)

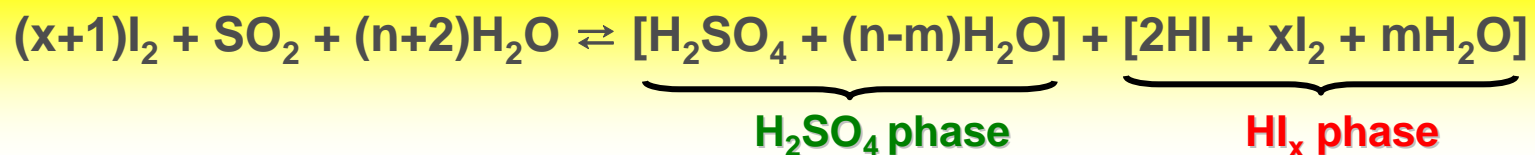


Bunsen with insoluble iodide/sulfate formation

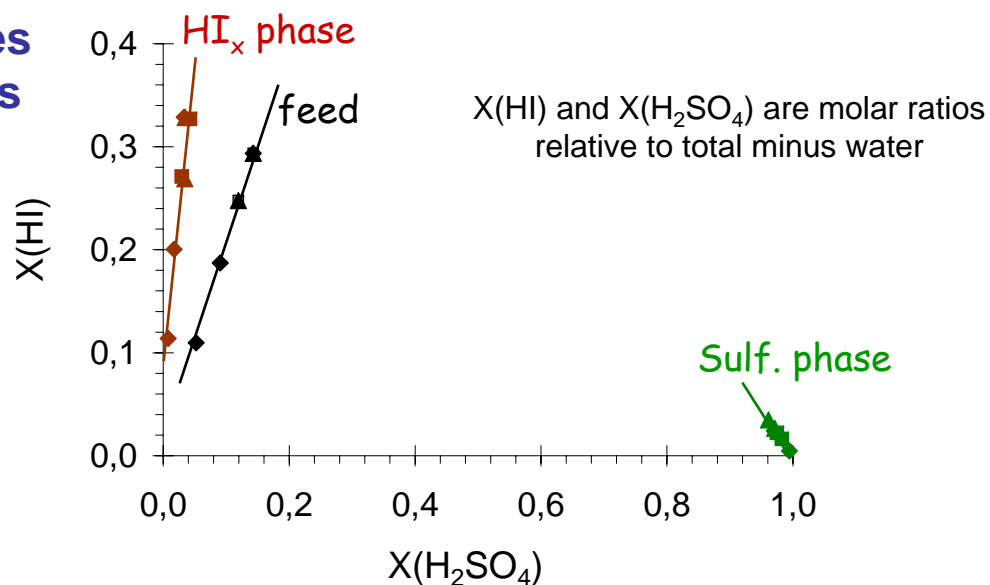
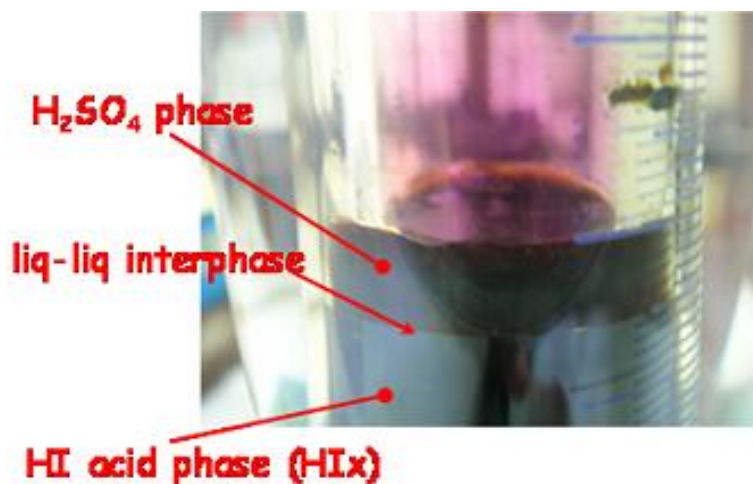


Giaconia A. *et al.* IHEC Istanbul (2007)

Characterization of liq-liq phase behavior of products

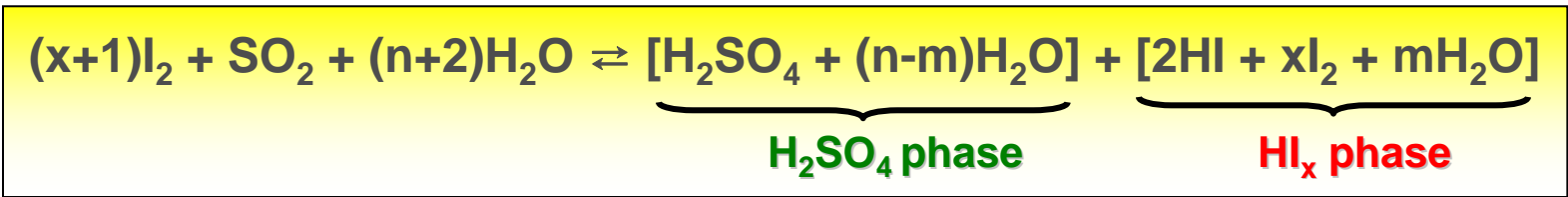


concentration and mutual
contamination of the two liquid phases
determined under different conditions



Giaconia A. *et al.* Int. J. Hydrogen Energy (2007)

Coupling with solar source and operation mode for the Bunsen reactor

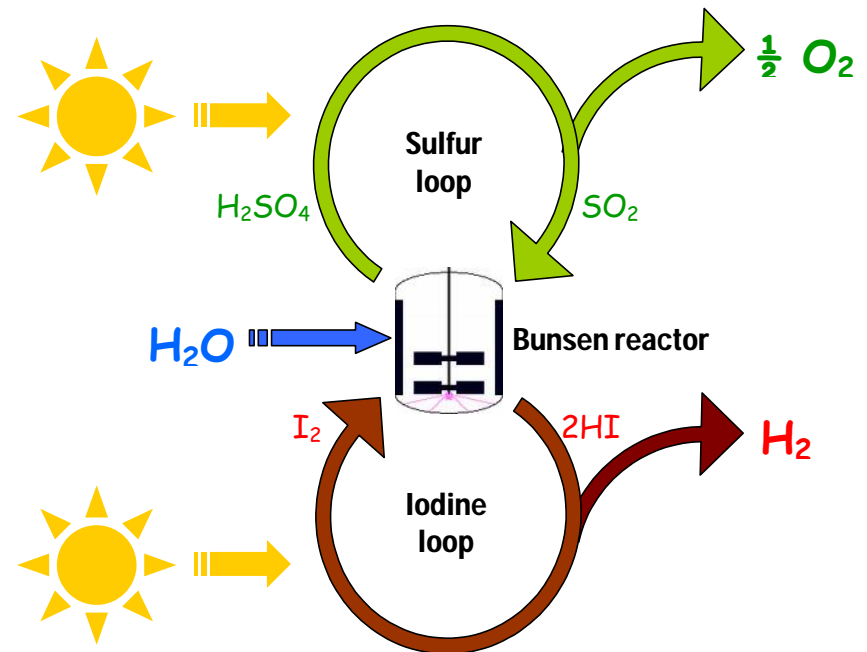


Bunsen reactor operation modes:

1. semi-continuous: following SO_2 production from solar reactor:
 HI_x phase / I_2 storage
2. continuous: SO_2/H_2SO_4 storage

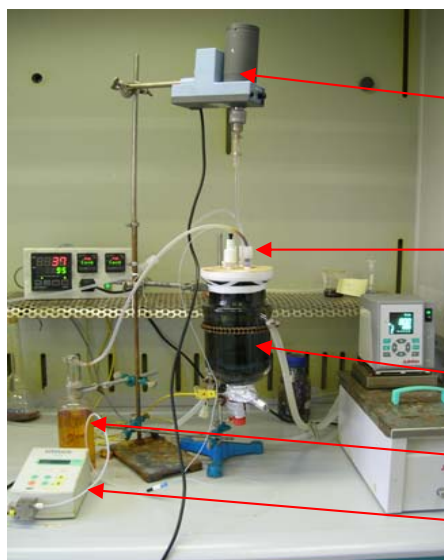
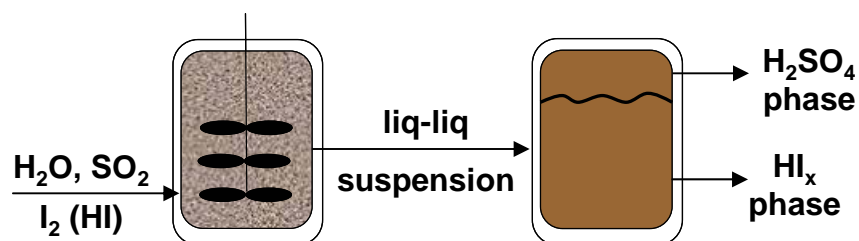
↓ very large I_2 inventory
required for semi-continuous
operation

Bunsen reactor continuous
operation is recommended also
for solar-powered S-I cycle



Possible configurations for continuous Bunsen reactor

Mixer + settler



agitator

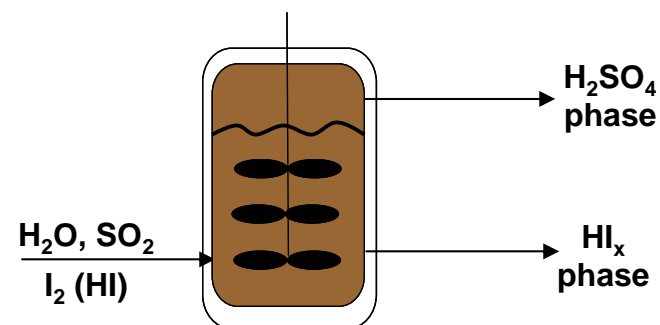
SO₂ inlet

mixed reactor

exit gas trap

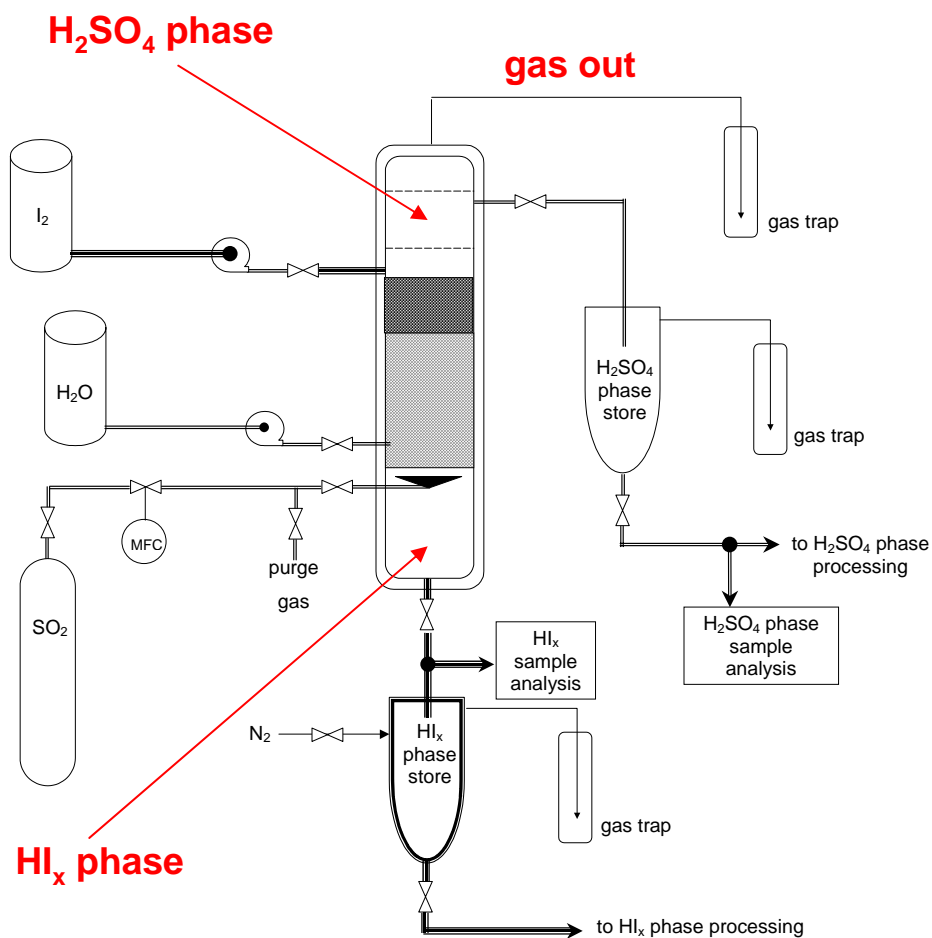
H₂O pump

Integrated mixer-settler



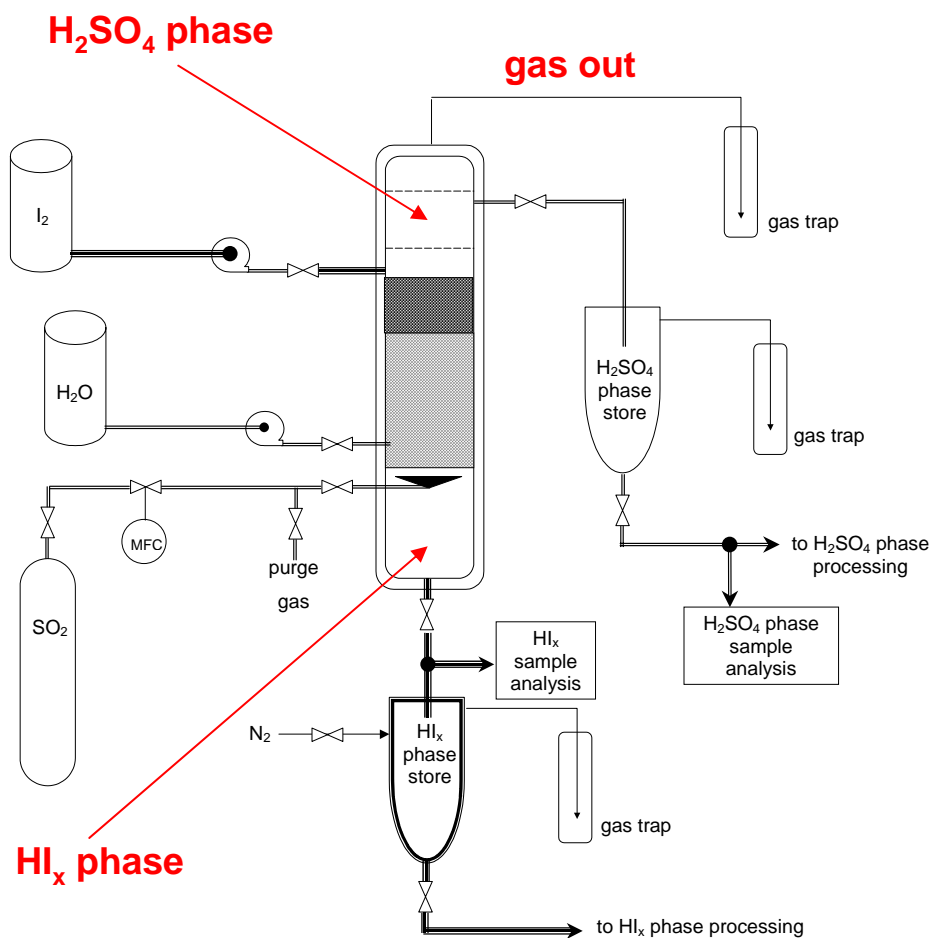
- reaction phase is the HI_x phase with the high I₂ concentration
- H₂SO₄ is continuously separated in the reactor

Integrated mixer-settler: lab apparatus (ca. 10 L/h SO_2)

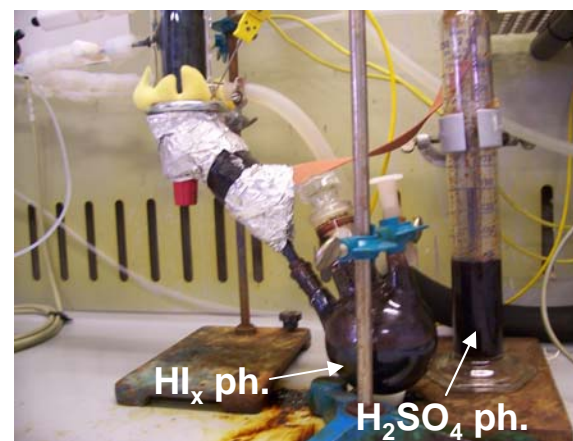
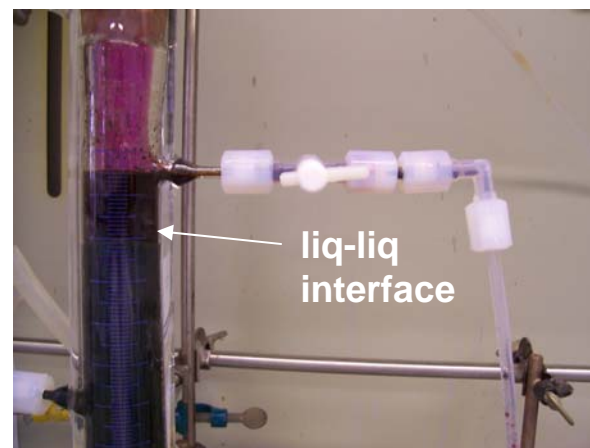
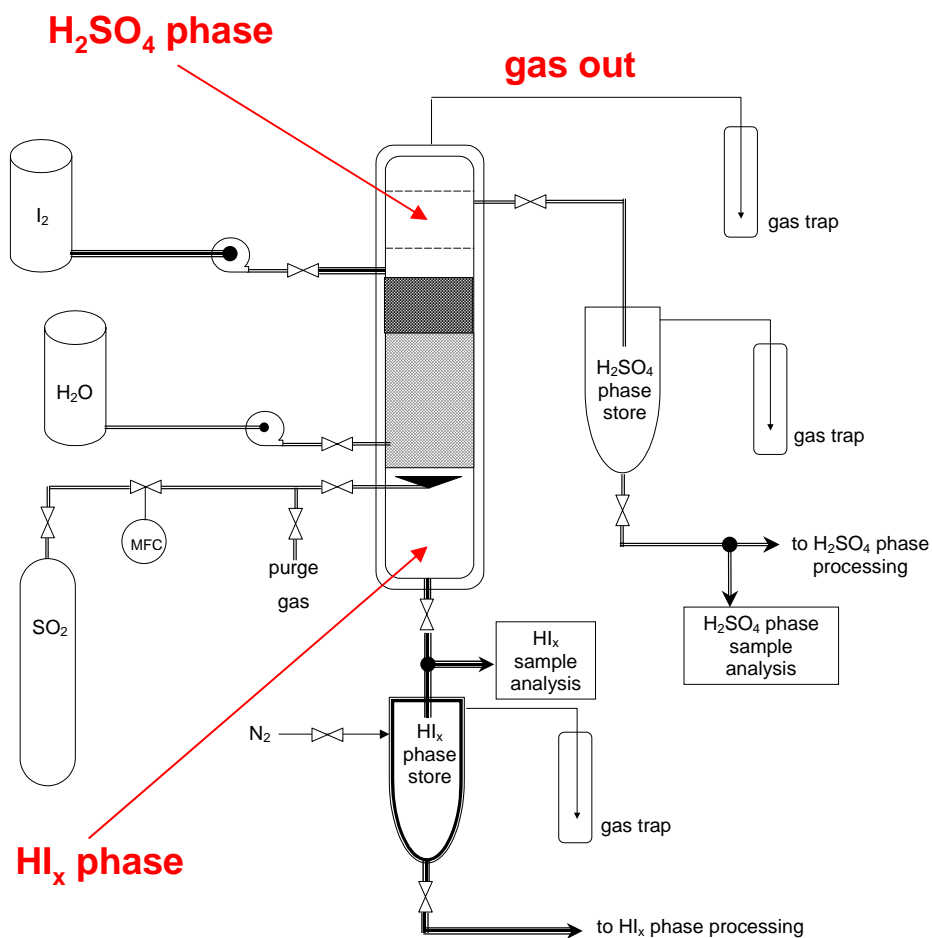


- packed column for SO_2 reactive adsorption (no mechanical mixing)
- SO_2 and H_2O (resp. I_2) fed below (resp. above) the packed bed
- H_2SO_4 phase continuously drained out near the top
- HI_x phase continuously drained out from the bottom through electrically traced pipes
- materials: glass and PTFE
- packing made of glass/tantalum rings (+ I_2 pellets)
- able to process SO_2 rates the order of 10 L/h
- fluid dynamics not optimized
- temperature controlled by water recirculation in the column jacket

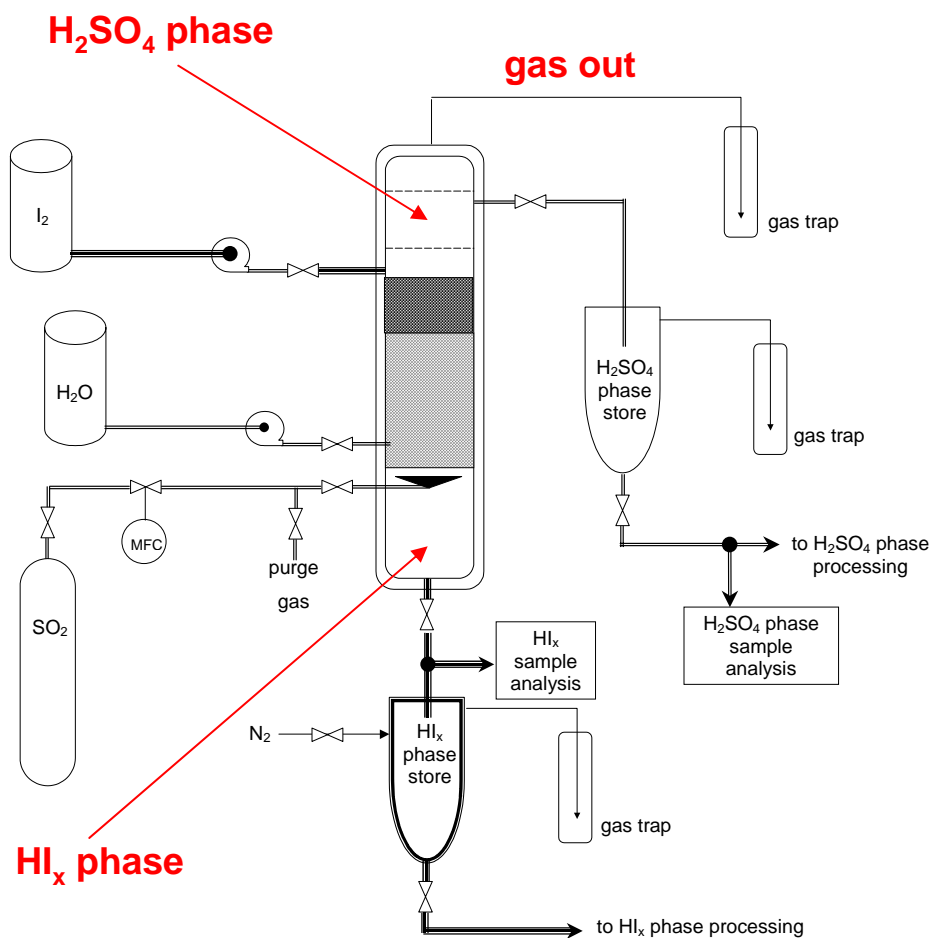
Integrated mixer-settler: lab apparatus (ca. 10 L/h SO₂)



Integrated mixer-settler: lab apparatus (ca. 10 L/h SO_2)



Integrated mixer-settler: lab apparatus (ca. 10 L/h SO_2)

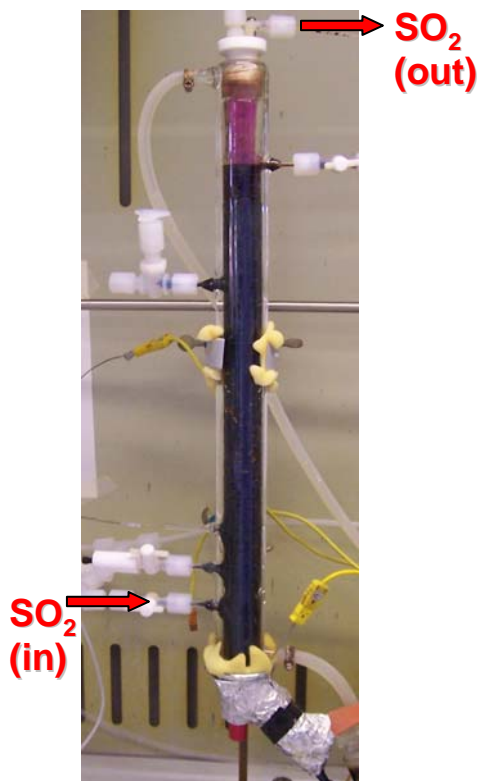


Procedure

1. SO_2 injection in a I_2 -saturated $HI/H_2O/I_2$ solution
2. Analysis of the SO_2 -saturated HI_x phase
3. Continuous feeding of $SO_2/H_2O/I_2$ at $80^\circ C$
4. Continuous removal of formed HI_x and sulfuric acid liquid phases
5. Reactor shut down and collected samples analysis
6. Collected liquid phases processing

Integrated mixer-settler: lab apparatus (ca. 10 L/h SO₂)

Start up



during start up loaded HI/H₂O/I₂ was saturated with SO₂ at 1 atm



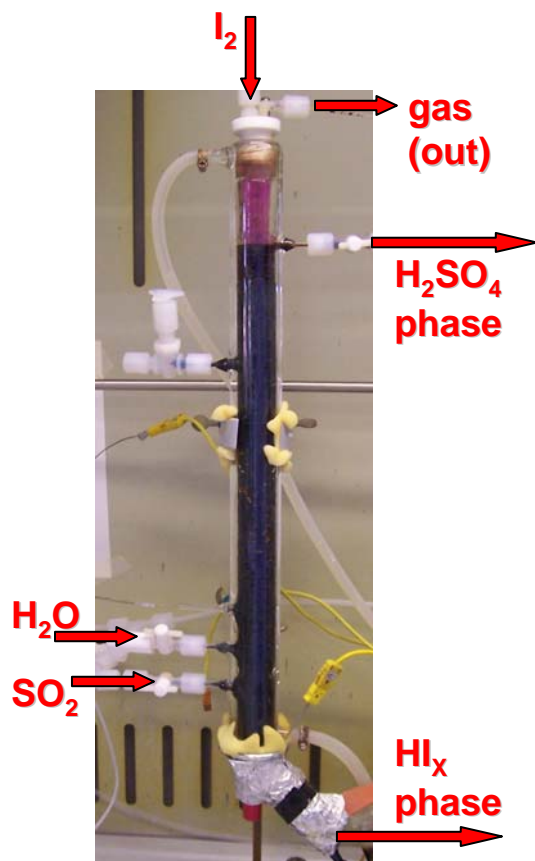
a single HI_x phase formed due of lack of H₂SO₄ hydration water

T	Entry	molar fractions in the saturated single HI _x phase			
		HI	H ₂ O	I ₂	H ₂ SO ₄ (+SO ₂)
77-80°C	1	0.13	0.51	0.34	0.02
	2	0.14	0.51	0.33	0.02
	3	0.14	0.51	0.33	0.02

minimum water at 80°C and SO₂ at 1 atm

Integrated mixer-settler: lab apparatus (ca. 10 L/h SO₂)

Continuous running:



Set temperature / pressure = 80°C / 1 atm

Continuous running time = 2 - 6 h

Water-to-SO₂ feed ratio = 10.55-13.47 mol/mol

Iodine-to-SO₂ feed ratio = 4.77-5.76 mol/mol

SO₂ feed = 4.7-5.0 NL/h

H₂O feed = 39.5-54.0 mL/h

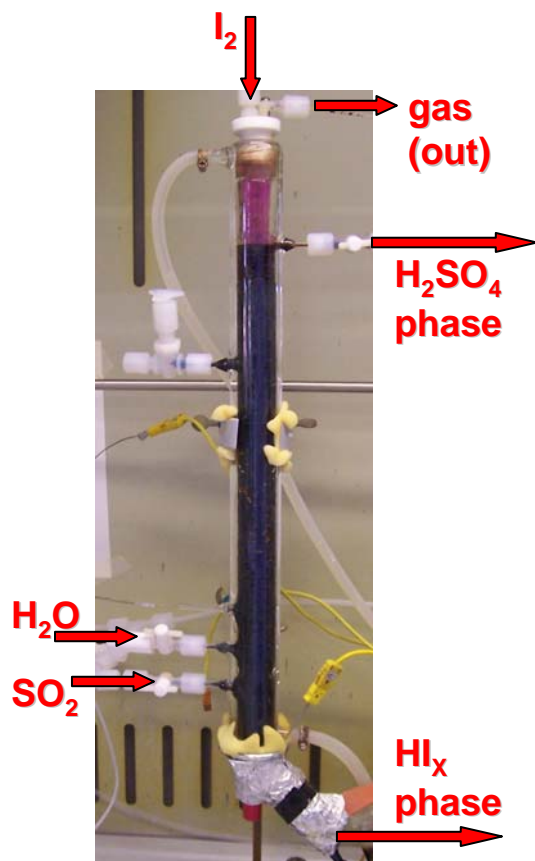
I₂ feed = 251.7-325.6 g/h

H₂SO₄ phase output = 20-21 mL/h

[H₂SO₄] = 49 - 56 wt%; % SO₂ adsorption = 97-98 %

Integrated mixer-settler: lab apparatus (ca. 10 L/h SO₂)

Continuous running:



composition of the collected H ₂ SO ₄ phase (molar fractions)			
HI	H ₂ O	I ₂	H ₂ SO ₄
0.01	0.84	< 0.01	0.15
< 0.01	0.80	< 0.01	0.19

I₂/SO₂ = 4.77
H₂O/SO₂ = 10.55

I₂/SO₂ = 5.76
H₂O/SO₂ = 13.47

composition of the collected HI _x phase (molar fractions)			
HI	H ₂ O	I ₂	H ₂ SO ₄ (+ SO ₂)
0.15	0.50	0.33 *	0.02
0.13	0.53	0.33 *	0.02

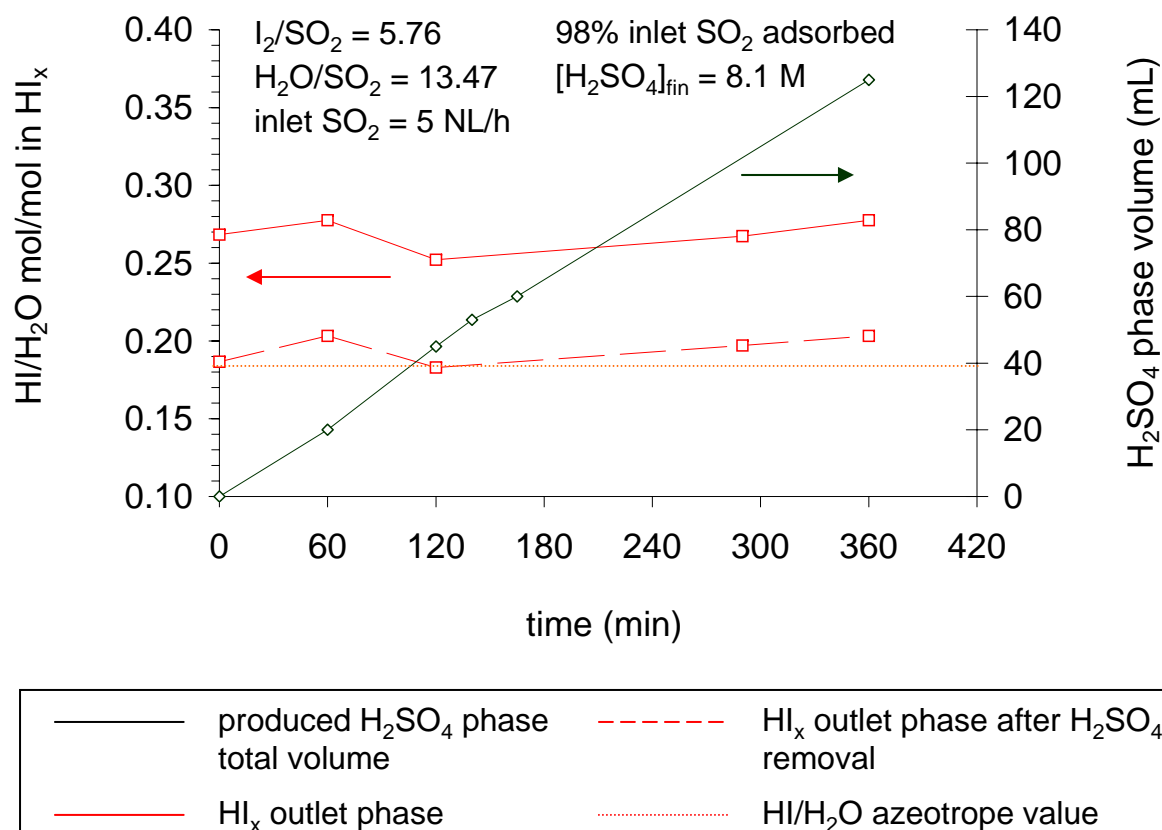
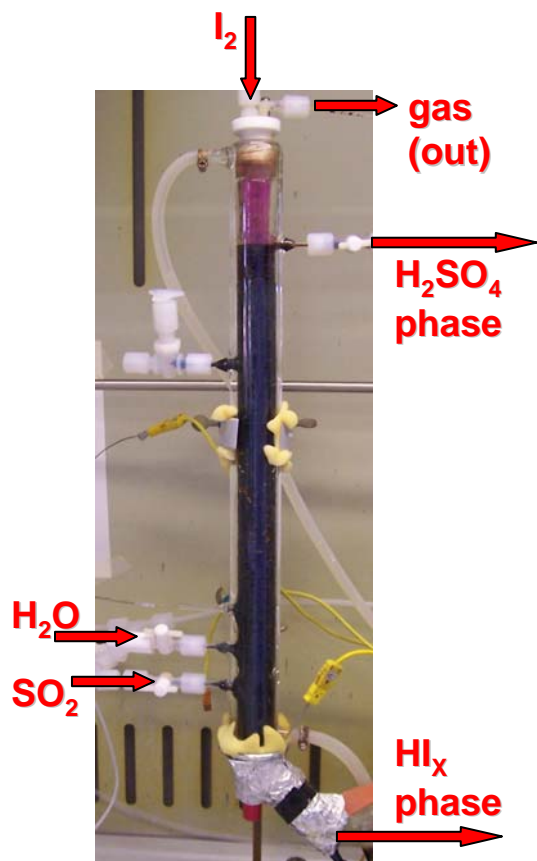
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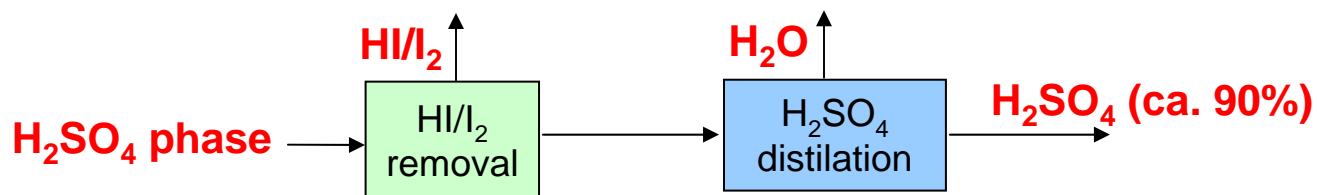
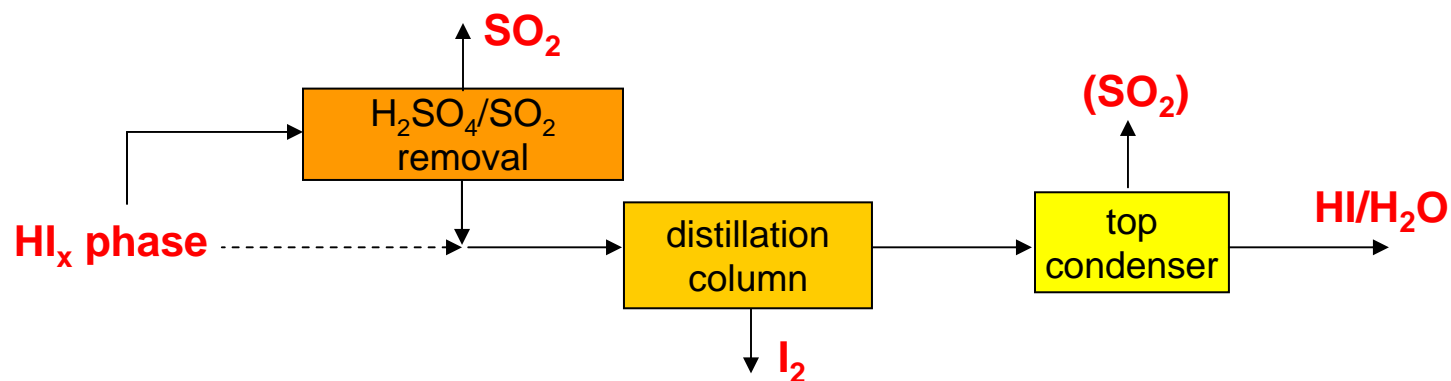
* solid I₂ persistent in the column: HI_x is always saturated with I₂

Integrated mixer-settler: lab apparatus (ca. 10 L/h SO₂)

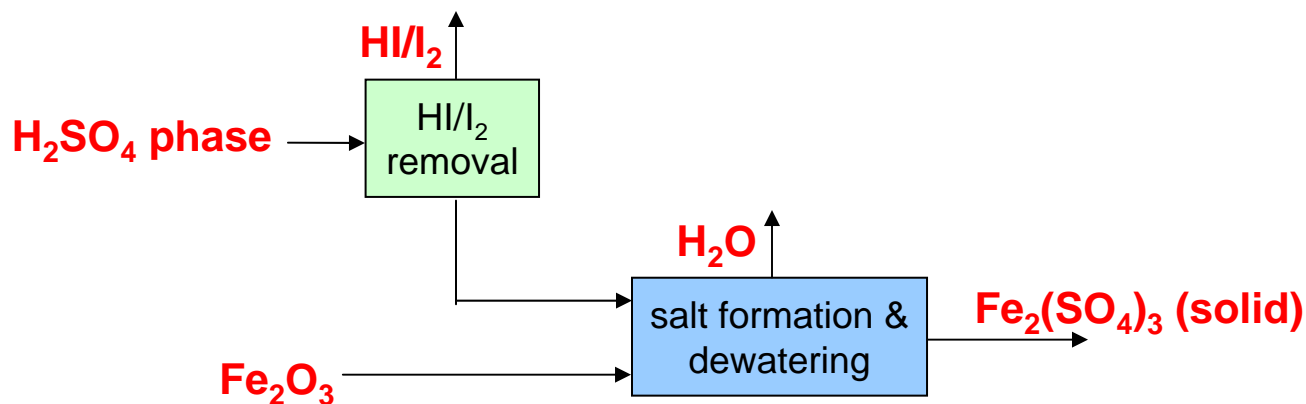
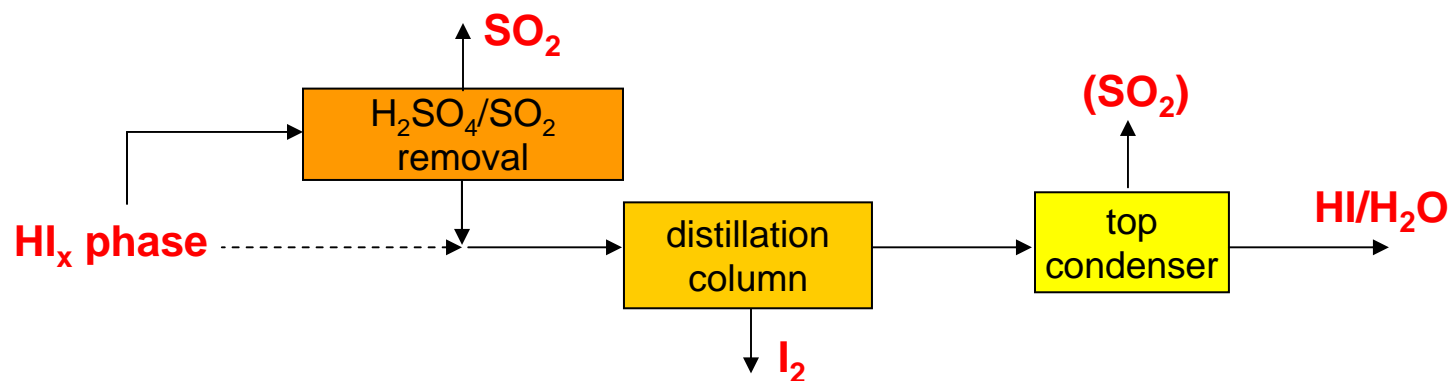
Continuous running:



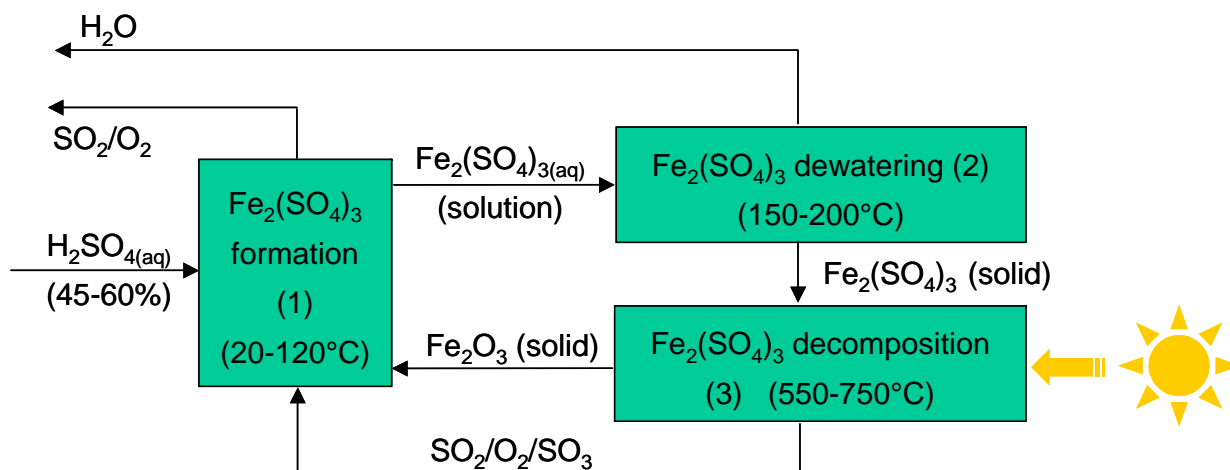
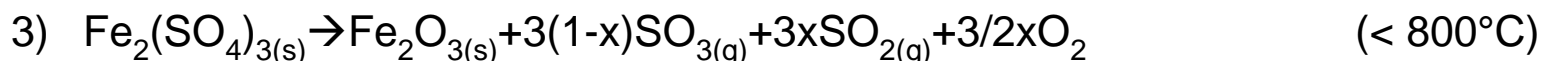
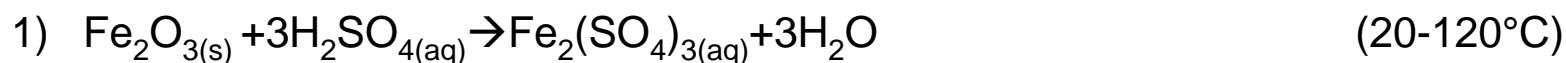
Continuous lab apparatus: acid phases processing



Continuous lab apparatus: acid phases processing

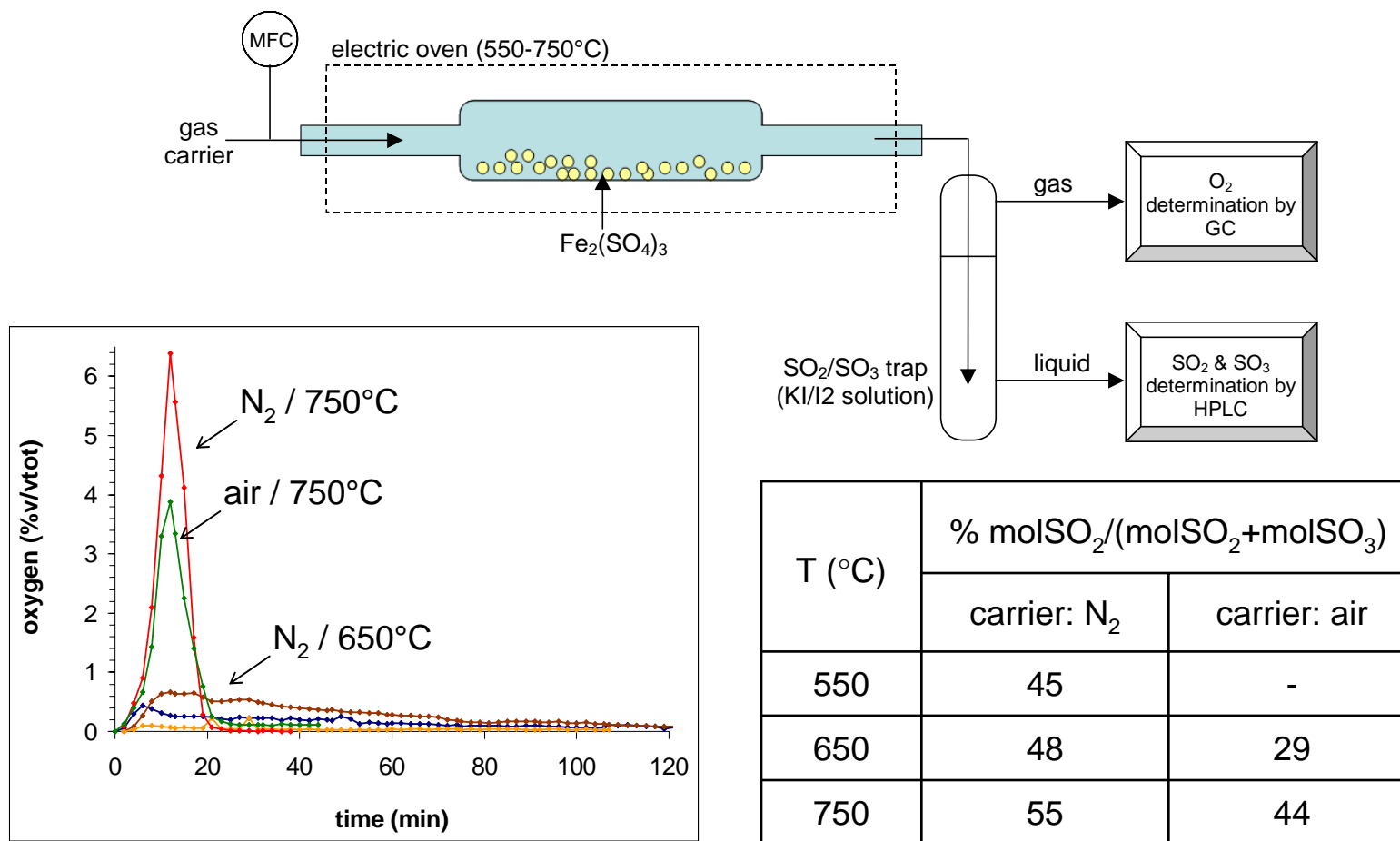


Use of Fe_2O_3 for H_2SO_4 solar splitting



1. lower maximum temperatures (< 800°C)
2. absence of catalysts
3. lower material corrosion
4. coupling with solar reactors feasible

Use of Fe_2O_3 for H_2SO_4 solar splitting



Conclusions and future work

- ✎ Different Bunsen reaction routes were investigated - reaction in water media first considered for small-scale closed-loop demonstration
- ✎ A reactive adsorption column proved suitable to obtain concentrated acid phases with compositions in good agreement with previous results on liquid-liquid phase behavior

next → evaluation of the effect of O_2 , temperature, H_2O -to- SO_2

next → comparison with other reactor configurations

- ✎ The possibility to use $Fe_2(SO_4)_3$ as intermediate recycling agent in the H_2SO_4 decomposition section was demonstrated

next → thermal analysis and technological feasibility assessment



Italian National Agency for New Technologies,
Energy and the Environment



Thermodynamic Solar Project

Thank You!