Evaluation of a *Continuous* Calcium-Bromine Thermochemical Cycle

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Project ID #
PD 16

OVERVIEW: Evaluation of a Continuous Ca-Br H_2 Cycle

Timeline

- Start – Oct 2005
- End – June 2006
- Complete: 75%

Budget

- Total project funding
  - DOE share 100%
- Funding FY05 $249K
- Funding FY06 $500K

Barriers

- Barriers addressed
  - Develop continuous process from batch
  - Improve H_2 yield from HBr
  - Integrate heat for higher efficiency

Partners

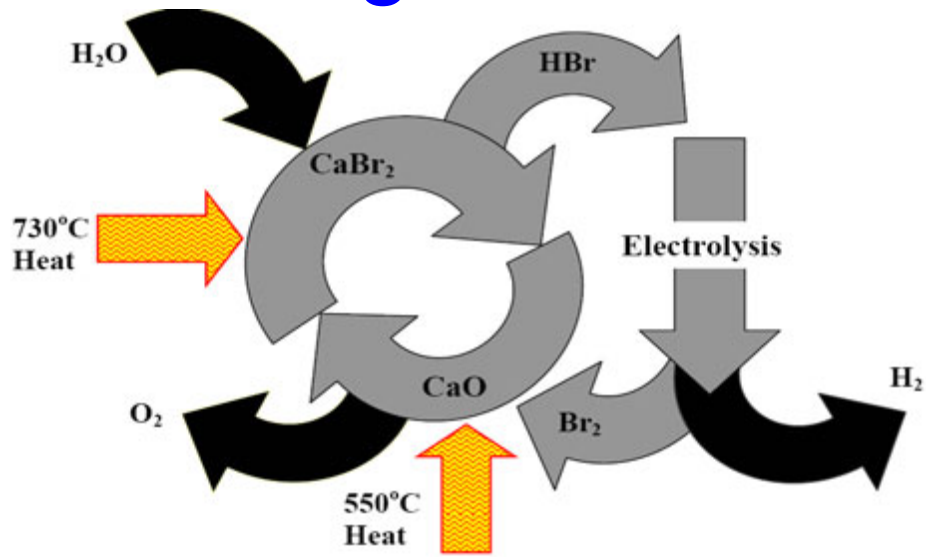
- University of South Carolina

OBJECTIVE: Evaluation of Continuous Ca-Br H_2 Cycle

Argonne will evaluate the Ca-Br cycle for H_2 and assess whether it is practical. The two focus areas of research during FY05:

- Argonne will examine cold plasma or electrolytic methods for the hydrogen generation as a replacement for the iron bromide/oxide reaction beds in the UT-3 cycle (earlier Japanese work),
- and also investigate the feasibility of a continuous molten spray reactor approach for the HBr generation step.

OBJECTIVE: Argonne Ca-Br looks to eliminate the last 2 stages of UT-3 cycle



[1] Water splitting with HBr formation (1000 K)

$CaBr_2 + H_2O \leftrightarrows CaO + 2HBr$

[2] Oxygen recovery (823 K)

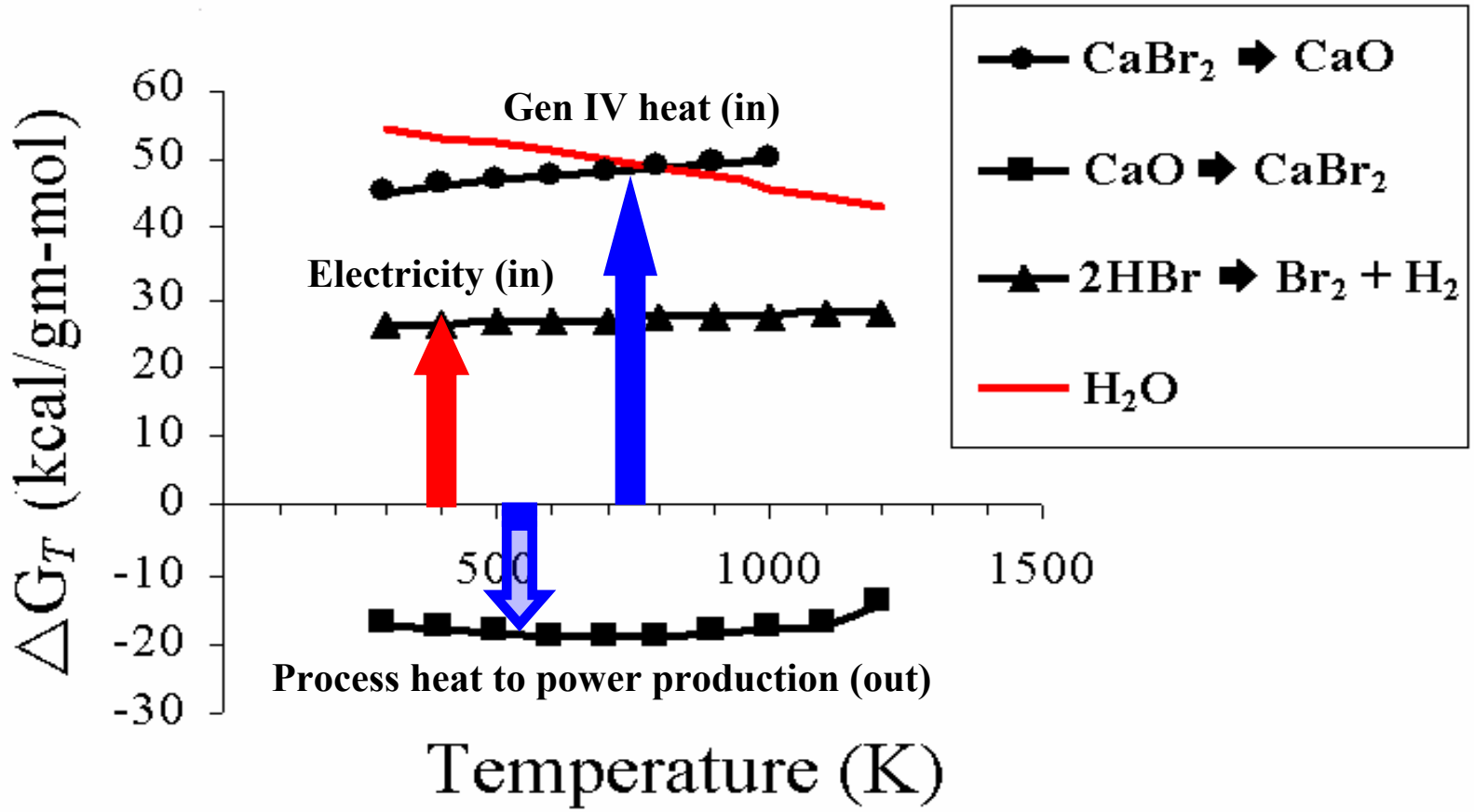
$CaO + Br_2 \leftrightarrows CaBr_2 + 0.5O_2$

[3] H_2 production and Br_2 regeneration (338 K)

PEM electrolysis or a non-thermal plasma will be used

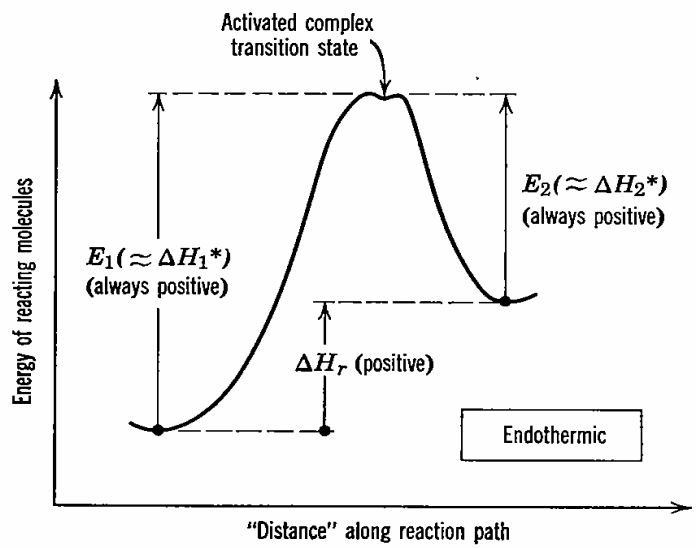
$2HBr + \text{plasma} \leftrightarrows H_2 + Br_2$

The overall goal – make the batch process continuous



$CaBr_2 + H_2O \rightarrow CaO + 2HBr$ is endothermic with $\Delta H_o = 43.38$ kcal gmol $^{-1}$ at 730°C

12.7 kcal/mol



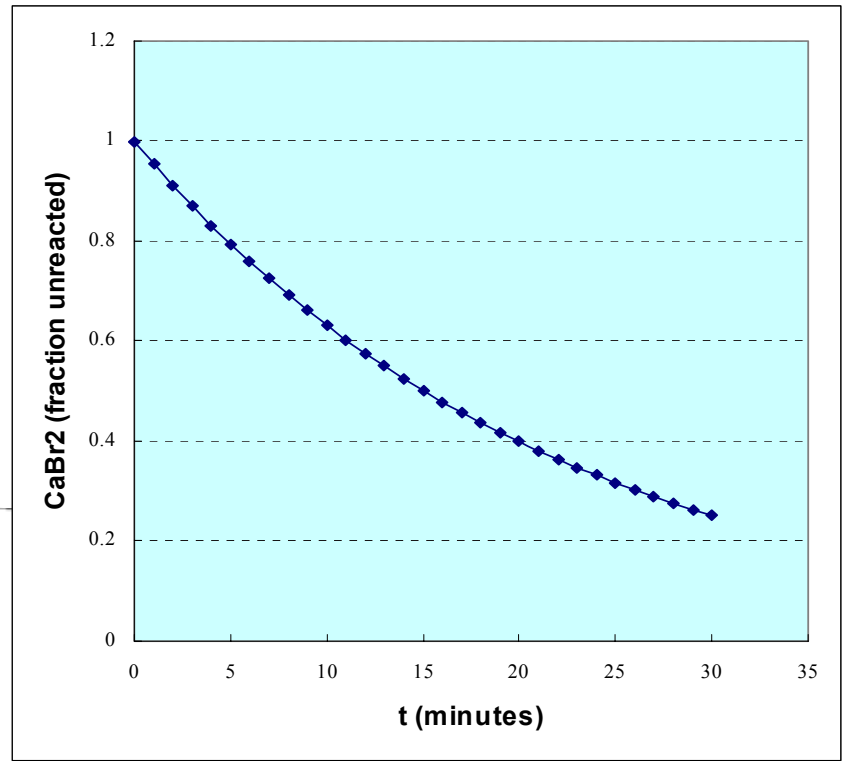
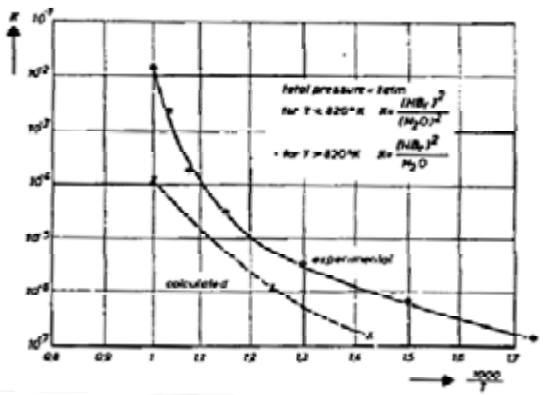


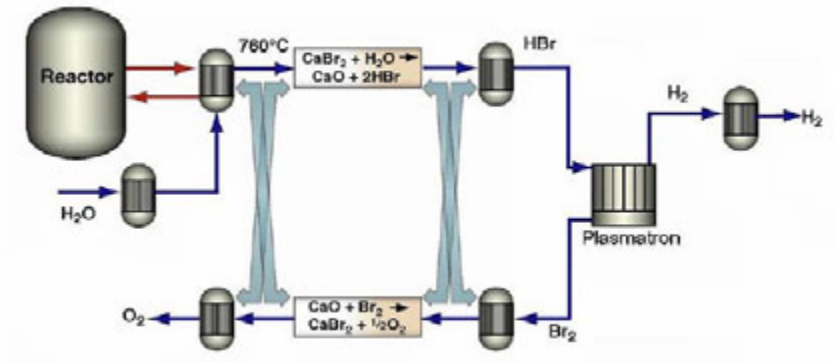
Fig. 4 Hydrolysis equilibrium constants as a function of temperature



Early $CaBr_2$ hydrolysis studies suggest that the some of the basic thermodynamic data needs refinement

$CaBr_2$ hydrolysis – kinetic data for 1st order reaction shows $E_a = 12.7$ kcal gmol^{-1} [53.1 kJ gmol^{-1}]

Argonne Modified *(from UT-3)* Calcium-Bromine cycle for Nuclear H_2



Advantages

✓ H_2 production continuous near ambient using plasmatron – alternative HBr from hot electrolysis (bench-tests) – and HBr PEM electrolysis (Weidner)

✓ H2 production at low temperature & low pressure worked synergistically with front end

✓ Process efficiency ~45%(no costs)

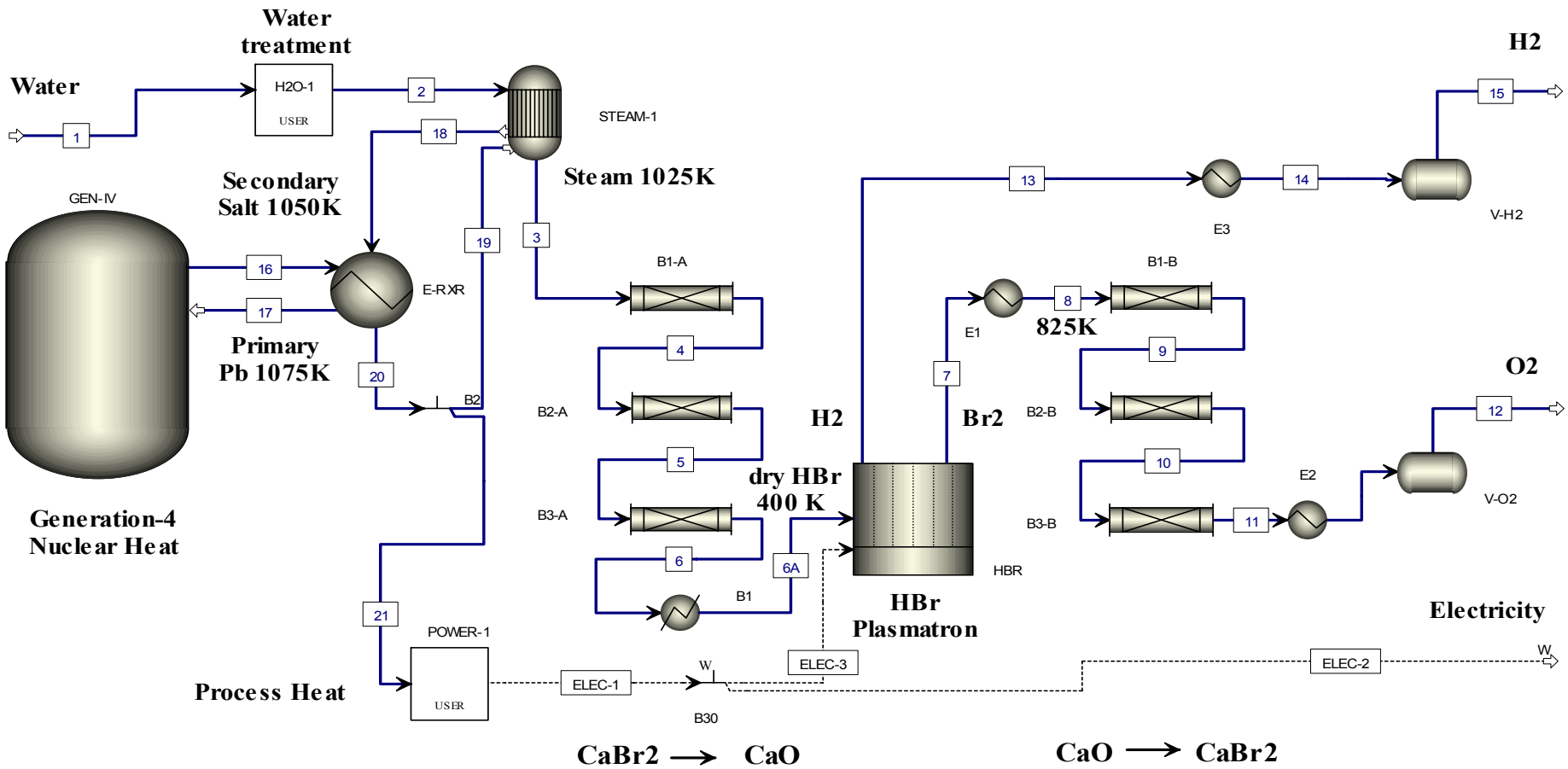
Disadvantages

✘ 72% volume change CaO → $CaBr_2$

✘ Br_2, O_2 at high temperatures (823K)

✘ Batch-staging still employed for Ca

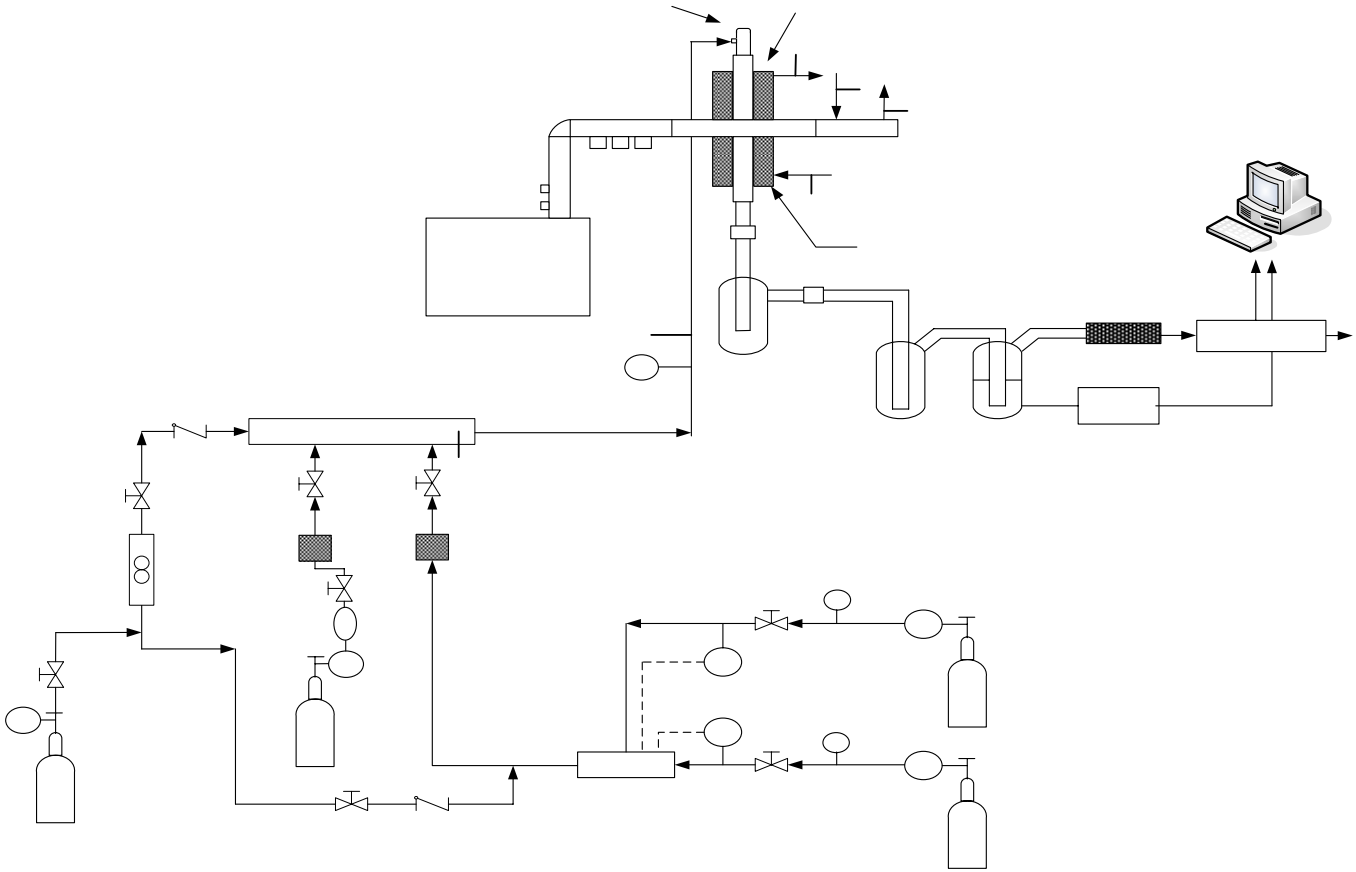
Process Design for the Ca-Br Cycle



Earlier studies with H_2S plasma-chemistry support investigation of $2HBr \rightarrow H_2 + Br_2$

- Plasma Chemical production of H_2 and Br_2 at low temperature and low pressure from HBr may show significant advantages over electrolysis.
- HBr has been *theoretically* studied by Nestor, et al.

Configuration for HBr Plasma-chemical experiments



Plasma chemical reactors adjust dimensions so that a resonant H_0 mode is established

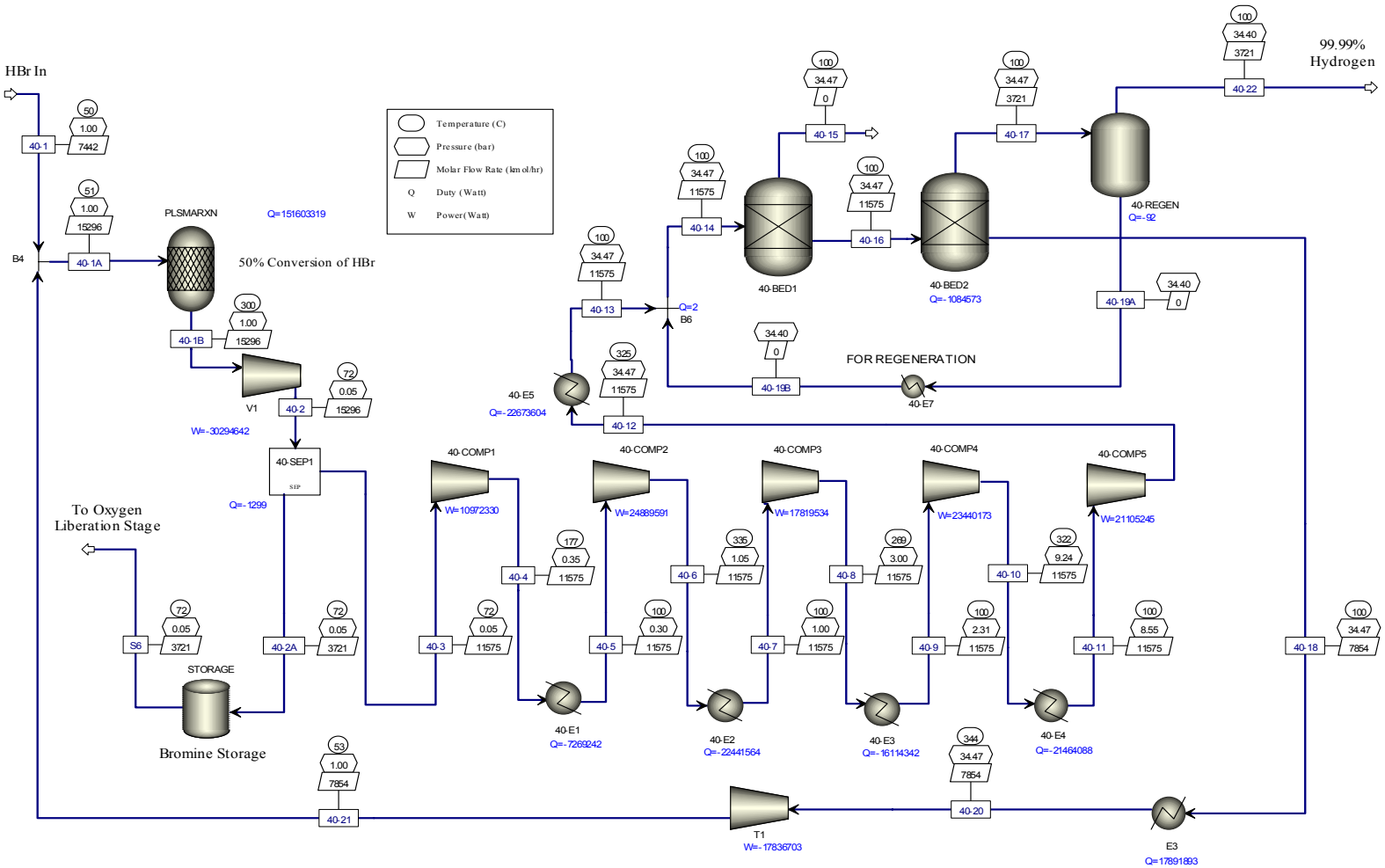
Cited from Buro R. Tschaggelar

http://www.ibrtses.com/simulations/microwaveresonator.html

Construction and pre-testing of an HBr cold plasma dissociation experiment apparatus

First successful test of non-thermal plasma generation on Argon gas at 10 l/min. The power draw was 350 Watts; 30-September 2005

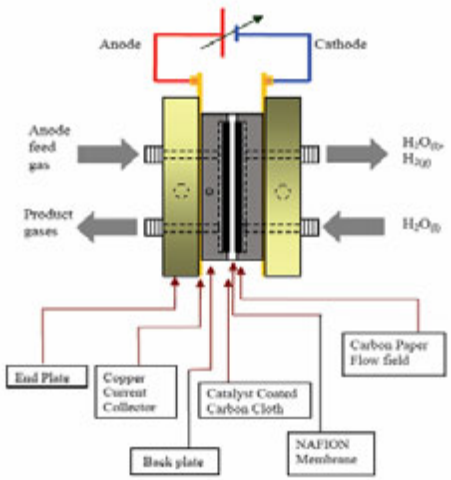
Plasmatron & H_2 compression to PSA and pipe. This route takes advantage of the low pressures that will favor the first stage hydrolysis reaction



Aspen Plus 11.1 Run:PSA 2003-09-13a 9/13/2003 9:42:00 AM

PEM electrolysis assembly for the production of hydrogen from HBr in the Ca-Br cycle as well as non-thermal plasma

John Weidner, U of South Carolina preprint for Intl. J. of Hydrogen Engineering shows excellent performance



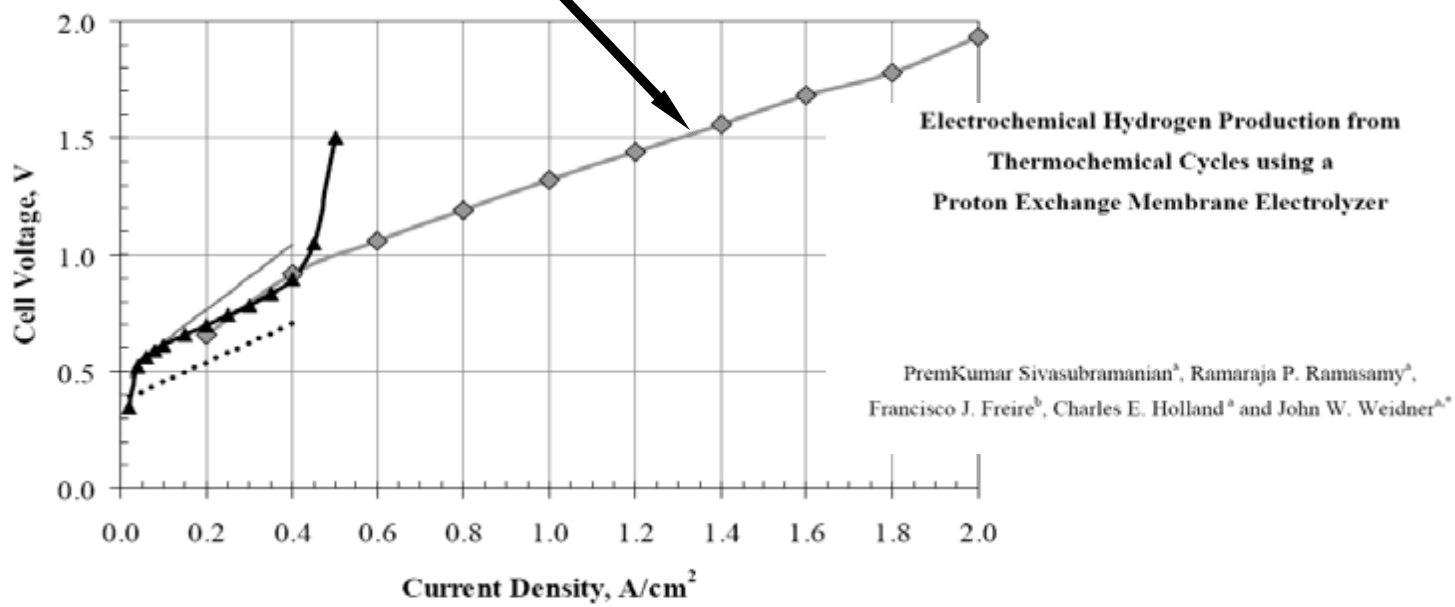
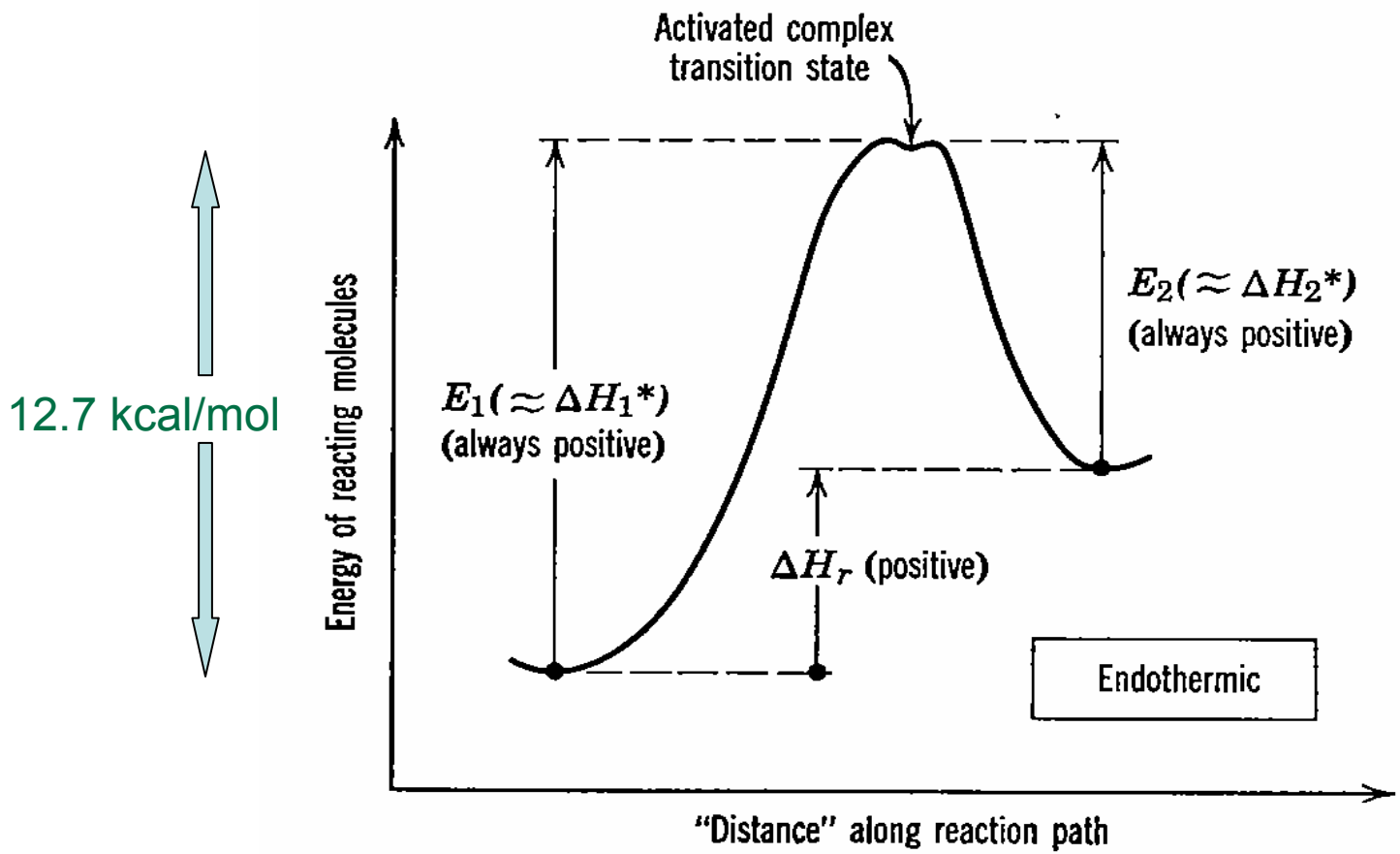


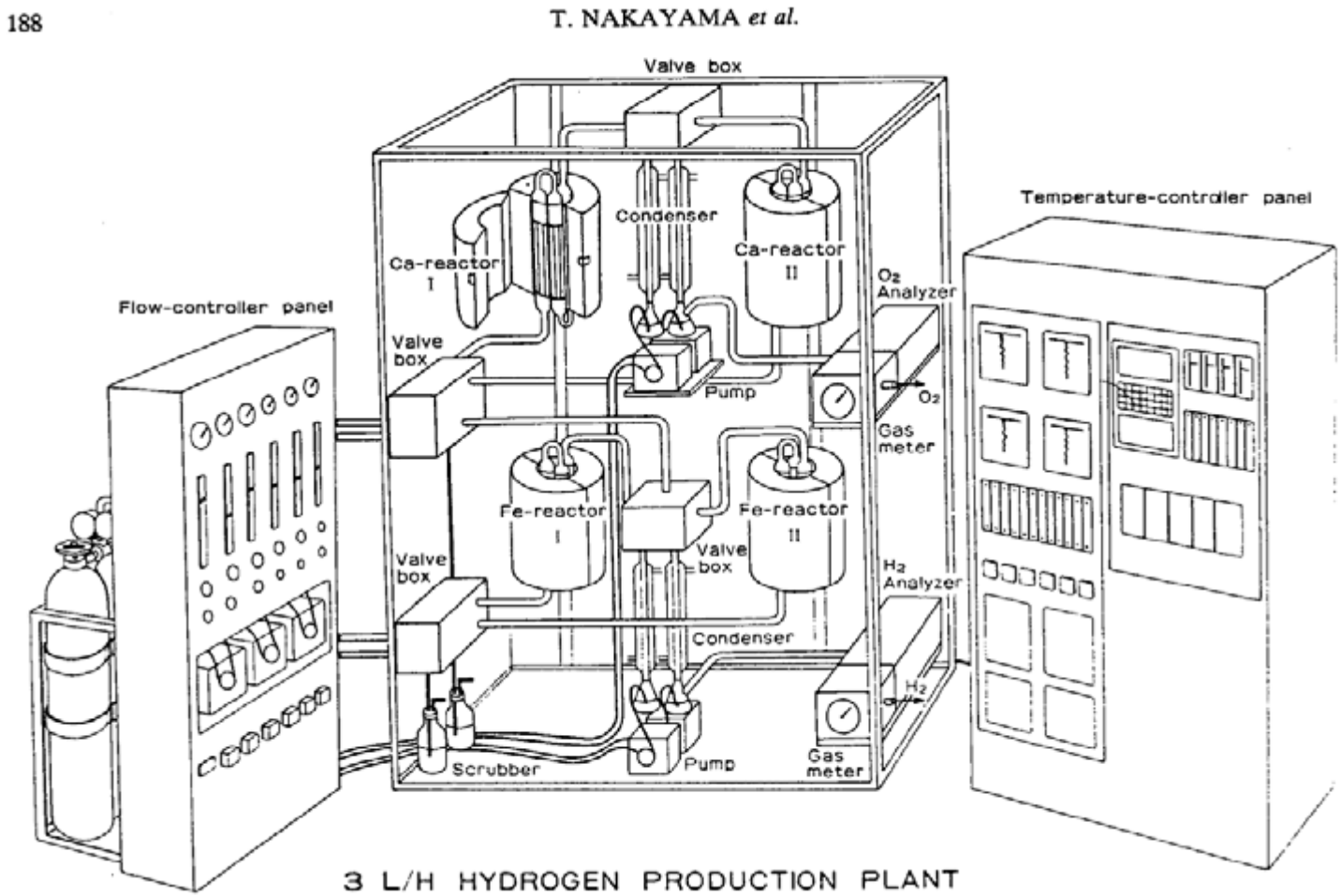
Figure 7: The current-voltage response for SO_2 (▲) and HBr (♦) electrolysis in a PEM electrolyzer. The results for the SO_2 electrolysis are the same as that given in Figure 5 but with a wider voltage scale. The HBr electrolyzer was operated at 80°C, 1.0 atm, and 50% conversion with a RuO_2 loading on the anode and cathode of 2.0 mg/cm^2.

$CaBr_2 + H_2O \rightarrow CaO + 2HBr$ is endothermic

$\Delta H_o = 43.38$ kcal gmol $^{-1}$



UT-3 efforts were always heat transfer limited, this means excess steam was the principal heat input [MASCOT facility- Nakayama, 1984]

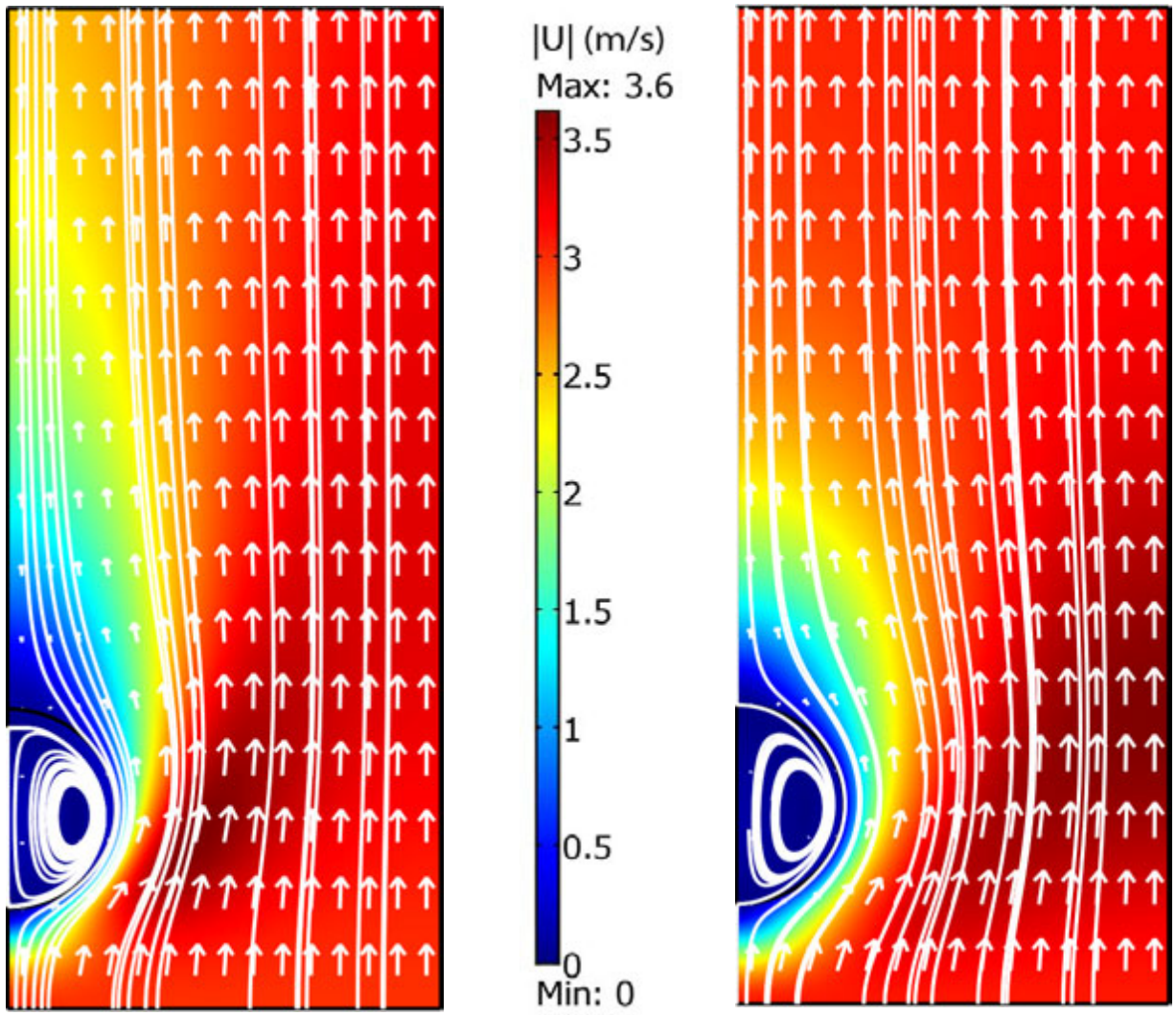


Initial $CaBr_2$ Droplet Model

Inlet velocity

3 m/s 1073 K steam

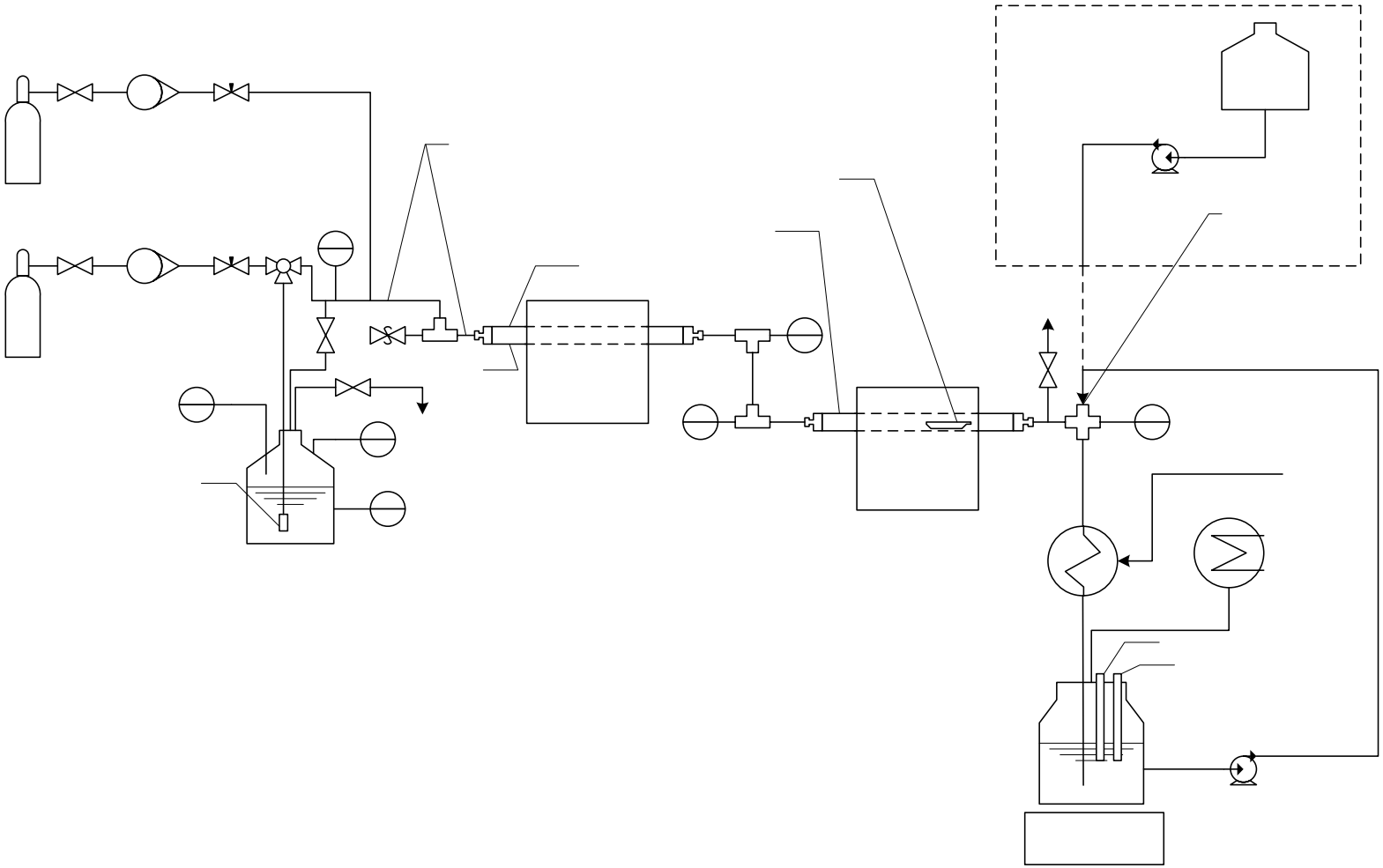
1 mm droplet Re=15



Color scale is velocity magnitude

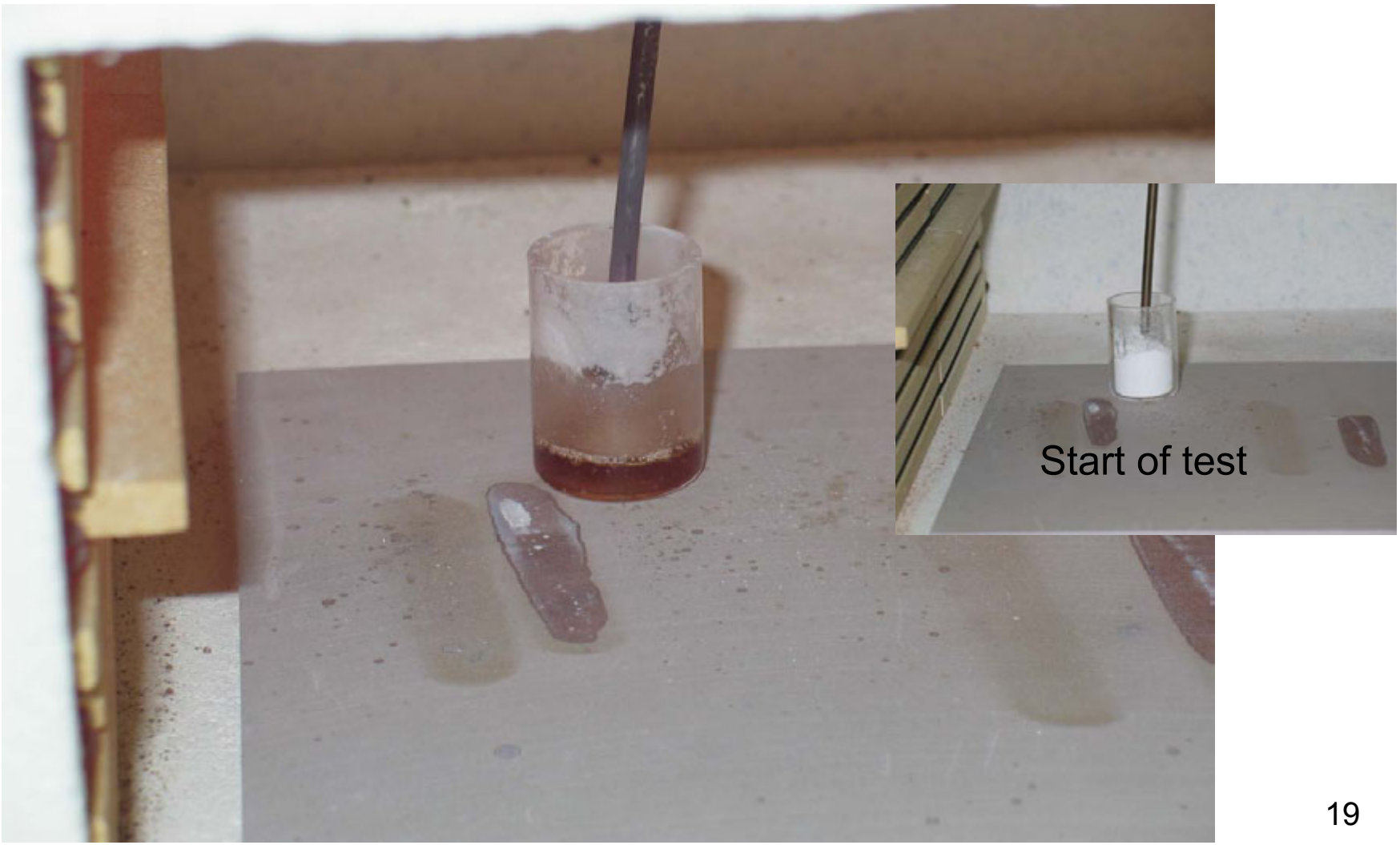
100 μm droplet Re= 1.5

$CaBr_2$ Hydrolysis will begin with steam reactions over unsupported $CaBr_2$



Propo

Anhydrous $CaBr_2$ melting ~780 ^oC after sparging He into melt



Technical Progress: Ca-Br-H_2O Efficiencies of 45% appear reasonable

Calcium-Bromine Water-splitting Cycle Heat Balance

Basis: 1,000 kg/hr H_2	T_{IN} (K)	T_{OUT} (K)	$MW_{Thermal}$ *IN*	*BRAYTON*	*REJECT*	*Efficiency* %	$MW_{Electric}$
10 - Reagent Steam	325	1050	4.765				
20 - [1] $CaBr_2 + H_2O \Rightarrow CaO + 2HBr$	1050	1000	32.677				
30 - [2] $CaO + Br_2 \Rightarrow CaBr_2 + 1/2O_2$	850	850		-7.900			-3.713
40 - [3] $2HBr \Rightarrow Br_2 + H_2$ (50% conversion)	350	600			-1.684	47.0%	13.471
40 - Plasmatron delivered power efficiency						75.0%	
40 - Compression for PSA	370	330	18.599		-11.073		
50 - Pressure Swing Adsorption - Recovery turbine							-2.257
60 - Electric Power Generation			18.022		-9.555	47.0%	-8.470
70 - Cooling Water	325	340					0.808
60 - Ancillary - controls, services, etc. (1.2%)							0.162
		SUM	74.063	-7.900	-22.311		0.000

Hydrogen Production (Lower Heating Value) = 33.333 MW_{Themal} *Efficiency* $_{Cycle}$ = 45.0%

NHI Calcium-Bromine Cycle

- The best portions earlier Ca-Br cycles have been refined by the current NHI program and will be retained
- Early thermodynamic and process design links have helped us to avoid some unproductive pathways
- Some basic thermodynamic data is still needed for Ca-Br but these problems are being understood (for example, the behavior of eutectic $CaBr_2$-CaO)
- HBr dissociation is practiced today using low-temperature electrolysis – two routes, a refined PEM cell are ready for laboratory testing

NHI Calcium-Bromine Cycle

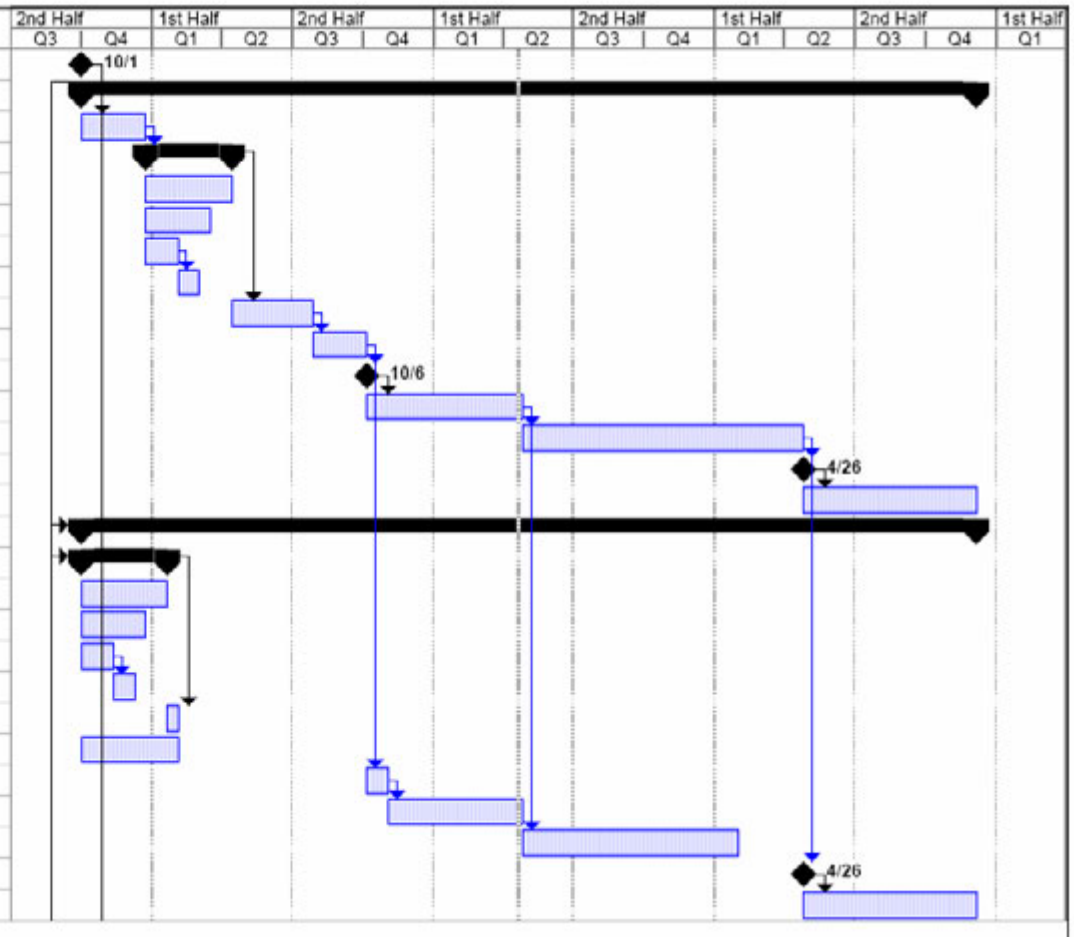
- While the supported Calcium system could be refined, we are pursuing a more aggressive development route looking at a continuous process
- Plasma H_2 recovery should avoid special materials the assembly and testing of the plasmatron is in good order It will be necessary to consider externalities – efficiencies of 45% are reasonable

Technical Accomplishments/ Progress/Results

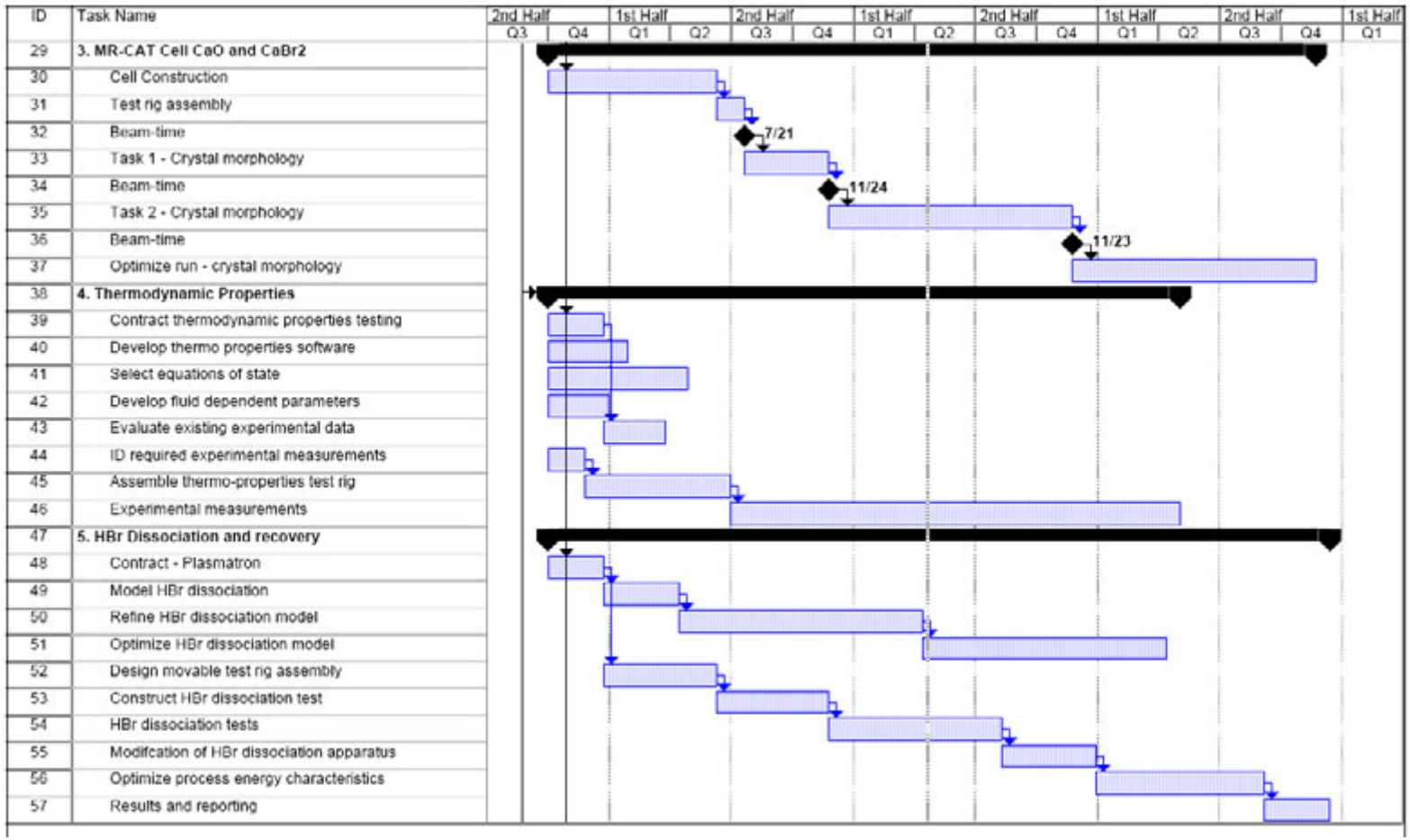
- All project efforts now focus on a continuous process to provide a better opportunity to meet the challenges of kinetics, materials, and operational issues using laboratory experiments
- Two laboratory routes to forming HBr (PEM and non-thermal plasma) are in the testing stage. Both of these show advantages over the UT-3 route
- A continuous process for molten $CaBr_2$ hydrolysis appears feasible laboratory construction is near complete for final testing
- High efficiencies appear reasonable

Ca-Br Future Plans

ID	Task Name
1	**Ca-Br TASK APPROVAL**
2	**1. Develop molten CaBr2 + steam reactor**
3	Contract - planning, materials
4	**Movable test-rig assembly**
5	Design and integration
6	Furnace
7	Piping
8	Instruments
9	Laboratory preparation - 1000 K steam
10	Spray-dryer assembly
11	First tests of CaBr2 + steam
12	A - CaBr2/Steam parametric tests
13	B - CaBr2/Steam - CaO separation & materials
14	CaBr2 design decision
15	CaBr2 optimization
16	**2. Develop CaO + Br2 regeneration**
17	**Movable test-rig assembly**
18	Design and integration
19	Furnace
20	Piping
21	Instruments
22	Shake-down testing
23	Analytical procedures
24	A - CaO + Br2 parametric tests (initial)
25	A - CaO + Br2 parametric tests (cont'd)
26	B - CaO/CaBr2 separation & materials
27	CaO design decision
28	CaO optimization

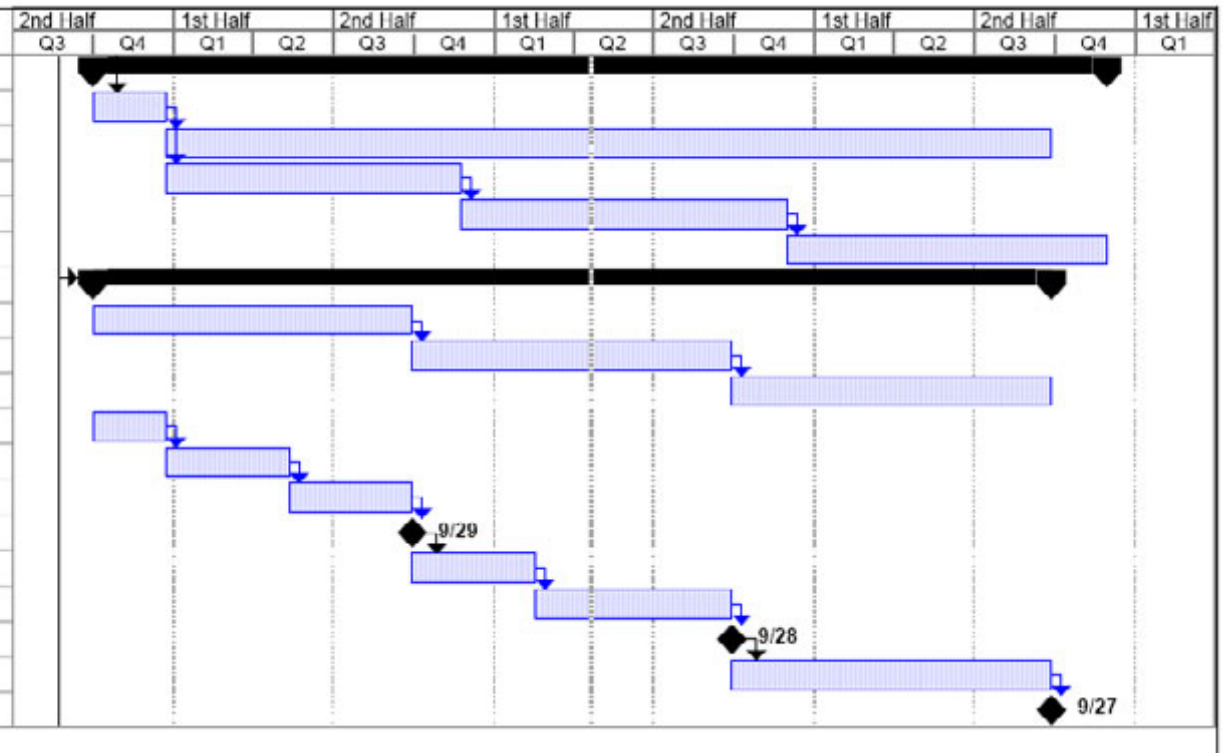


Ca-Br Future Plans



Ca-Br Future Plans

ID	Task Name
58	**6. Heat Transport & CFD**
59	Contract - Molten salt heat transfer
60	Evaluate heat transport
61	Develop CFD/heat transport experiments/model
62	Refine CFD/heat transport experiments/model
63	Optimize CFD/heat transport experiments/model
64	**7. Materials and Components**
65	ID materials and components issues
66	Refine materials and components issues
67	Recommended materials & components
68	Design materials test apparatus
69	Assemble materials test rig
70	Materials testing
71	Initial Review of Materials
72	Complete screening studies
73	Proof-testing apparatus
74	Downselect materials
75	Engineering performance
76	Final recommendation



Recent Publications

1. James Sienicki, David Wade, Anton Moisseytsev, Won Sik Yang, Sang-Ji Kim, Michael Smith, Gerardo Alberti, Richard Doctor, Diana Matonis, "Hydrogen/Power Plant Design – STAR Performer," Nuclear Engineering International, **50**:612 (July 2005).

2. Doctor, R.D., D.T. Matonis and D.C. Wade, *Hydrogen Generation Using a Calcium-Bromine Thermochemical Water-Splitting Cycle*, OECD NUCLEAR ENERGY AGENCY, Nuclear Science Committee, Second Information Exchange Meeting on Nuclear Production of Hydrogen, Argonne National Laboratory, Illinois, USA (2 - 3 October 2003); printed in Nuclear Production of Hydrogen, NEA No. 5308 (2004).

3. Wade, D.C., R. D. Doctor, J. J. Sienicki, D.T Matonis, R.S. Faibish and A.V. Moisseytsev, *STAR-H2: A Long-Refueling Interval Battery Reactor for Hydrogen and Water Supply to Cities of Developing Countries*, 5th International Conference on Nuclear Option in Countries with Small and Medium Electricity Grids, Dubrovnik, Croatia (May 16-20, 2004).

4. Doctor, R.D., D.T. Matonis, D.C. Wade, A.V. Moisseytsev, J.J. Sienicki, and R.S. Faibish, *STAR-H2 with a Calcium-Bromine Cycle: Delivering Hydrogen, Electricity and Water from a Modular Reactor Preliminary Design for a 5-MW Test System*, American Institute of Chemical Engineering 2004 Spring National Meeting, Session: 14004. Novel Hydrogen Generation Processes and Energy Applications IL, New Orleans, LA (April 25-29, 2004).

5. Doctor, R.D., D.T. Matonis, and D.C. Wade, *Hydrogen Generation Using a Calcium-Bromine Thermochemical Water-Splitting Cycle*, Symposium on Nuclear Energy and the Hydrogen Economy – Sponsored by MIT Center for Advanced Nuclear Energy Systems, Cambridge, MA (Sept. 23-24, 2003).