Evaluation of a *Continuous* Calcium-Bromine Thermochemical Cycle

Richard D. Doctor
Argonne National Laboratory

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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

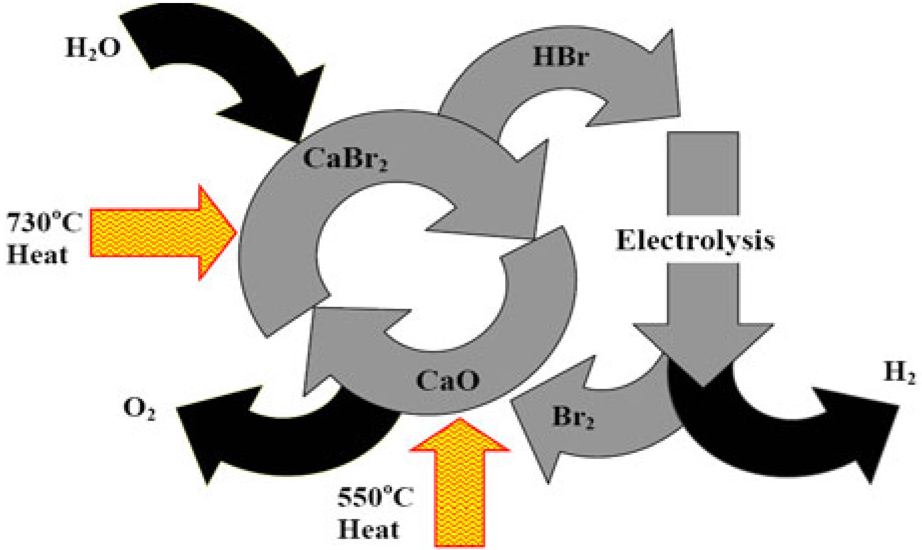
- University of South Carolina

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)

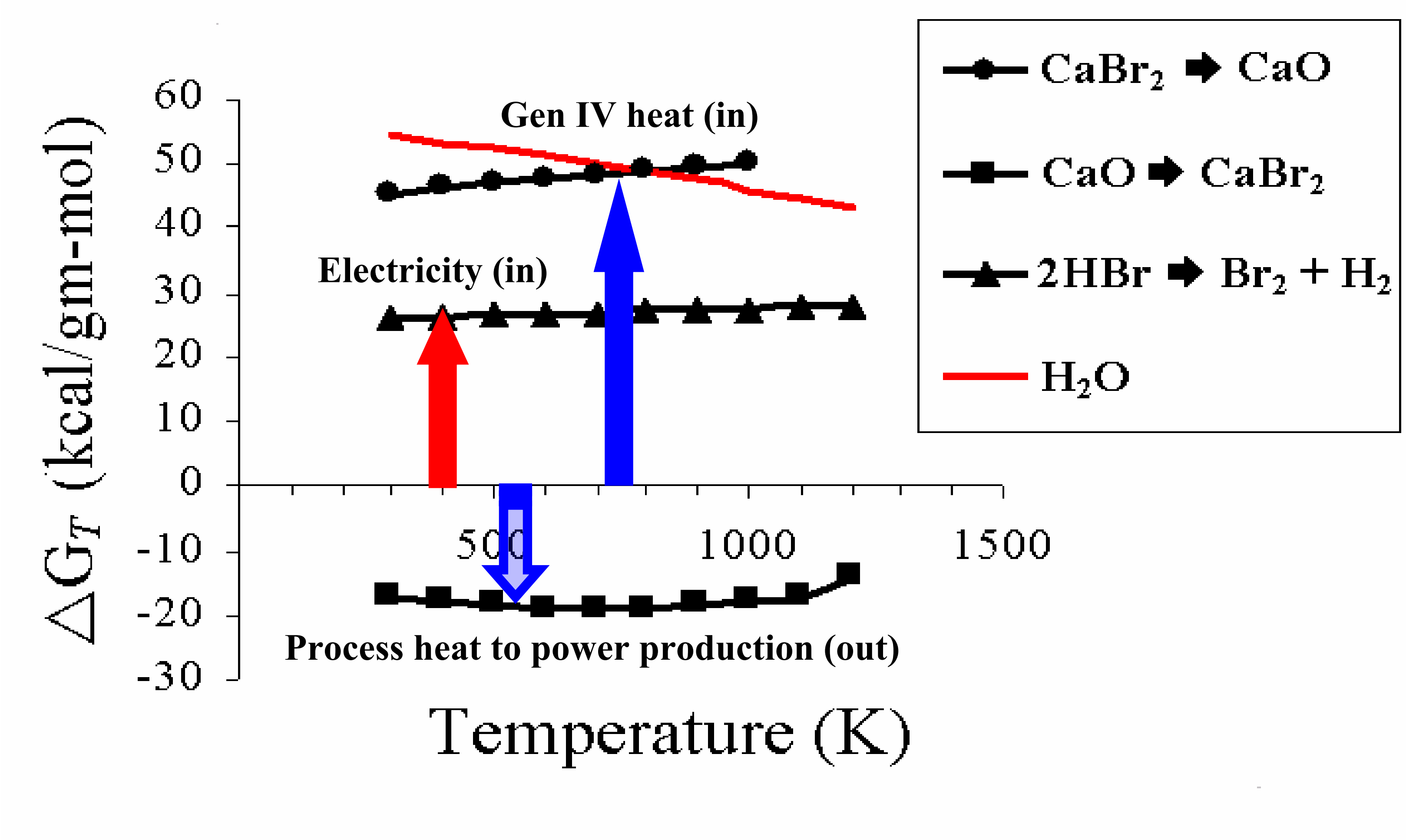
$CaO + Br_2 \leftrightarrows CaBr_2 + 0.5O_2$

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

PEM electrolysis or a non-thermal plasma will be used

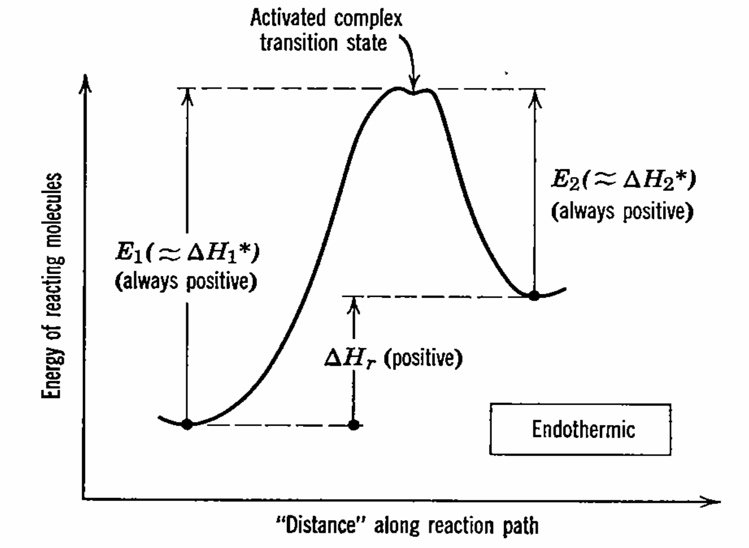
$2HBr + plasma \leftrightarrows H_2 + Br_2$

The overall goal – make the batch process continuous



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

12.7 kcal/mol



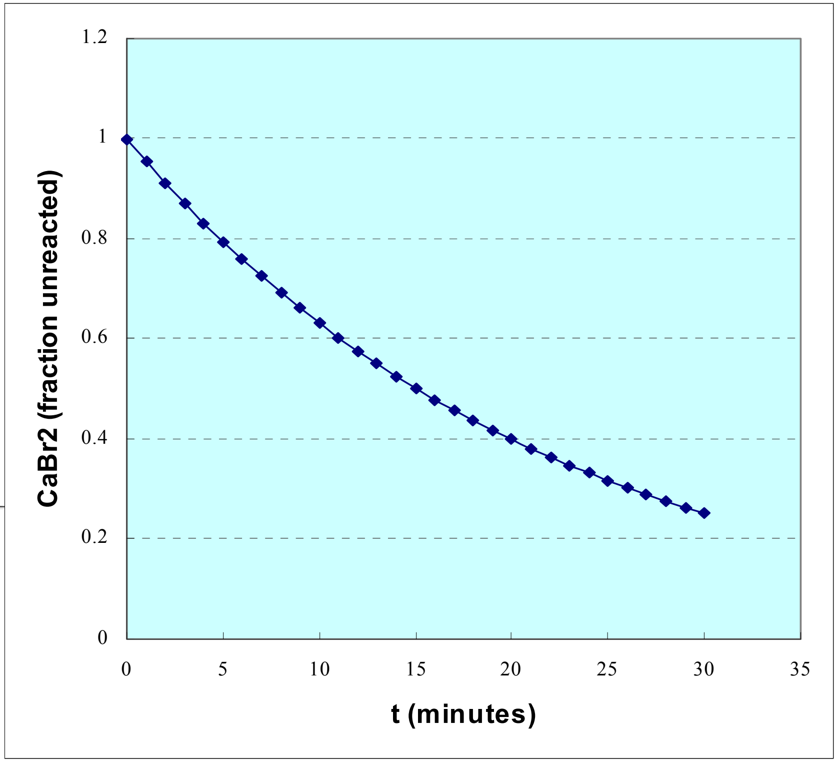
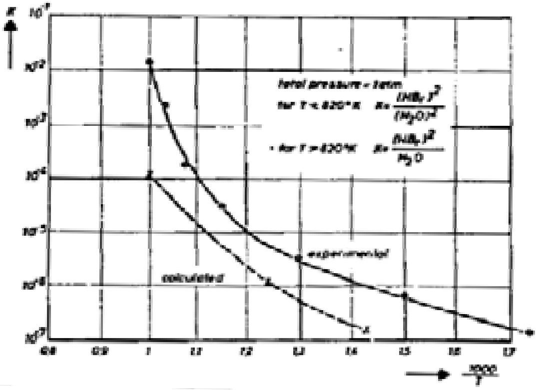


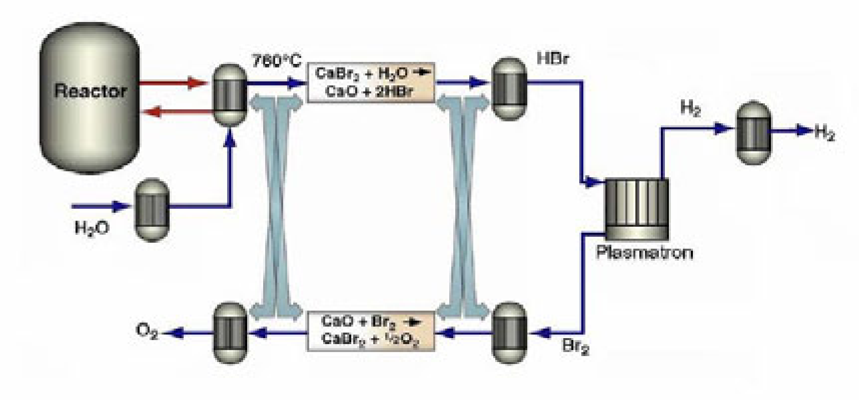
Fig. 4 Hydrolysis equilibrium constants as a function of temperature



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)

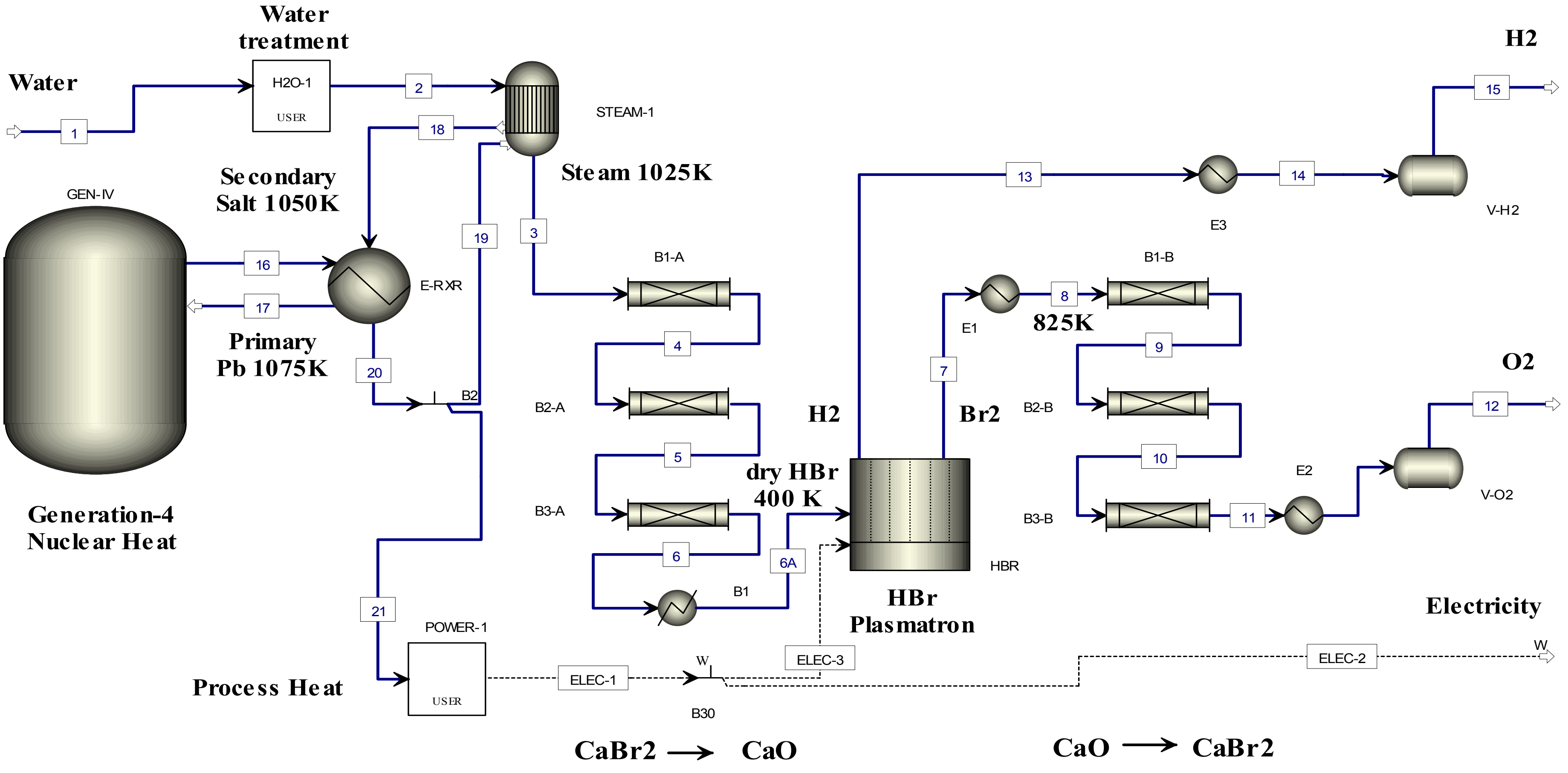
Disadvantages

✘ 72% volume change $CaO \rightarrow CaBr_2$

✘ Br_2, O_2 at high temperatures (823K)

✘ Batch-staging still employed for Ca

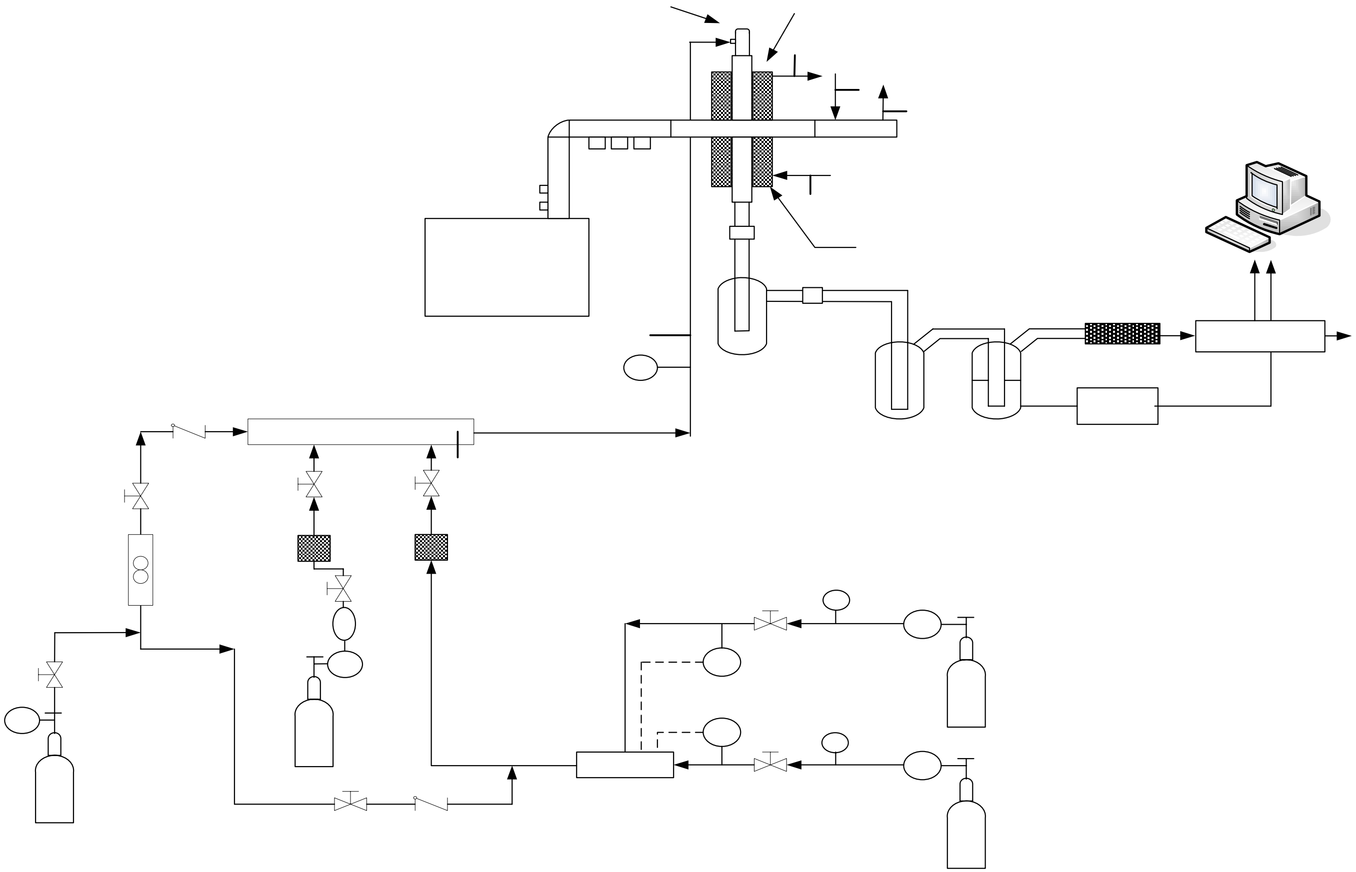
Process Design for the Ca-Br Cycle



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

```
Type         = H-Field (peak)
Monitor      = h-field (f=93.45) [1]
Component    = Abs
Plane at x   = 0
Frequency    = 93.45
Phase        = 270 degrees
Maximum-2d   = 698.98 A/m at 0 / 2.60307 / 0.574316
```

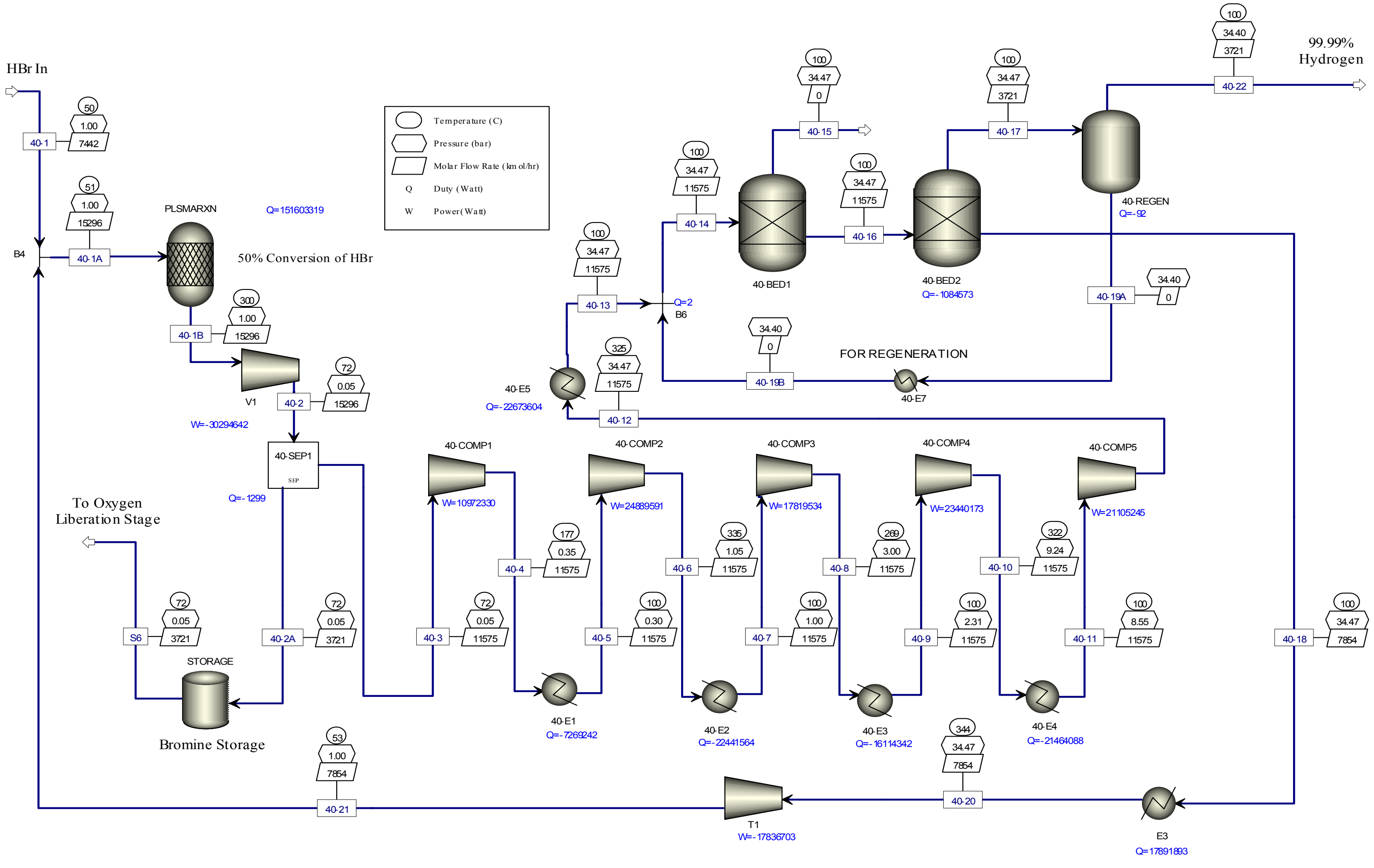
Cited from Buro R. Tschaggelar

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

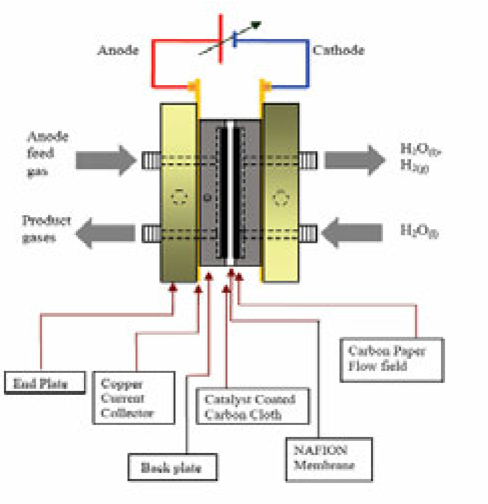
Plasmatron & H_2 compression to PSA and pipe. This route takes advantage of the low pressures that will favor the first stage hydrolysis reaction

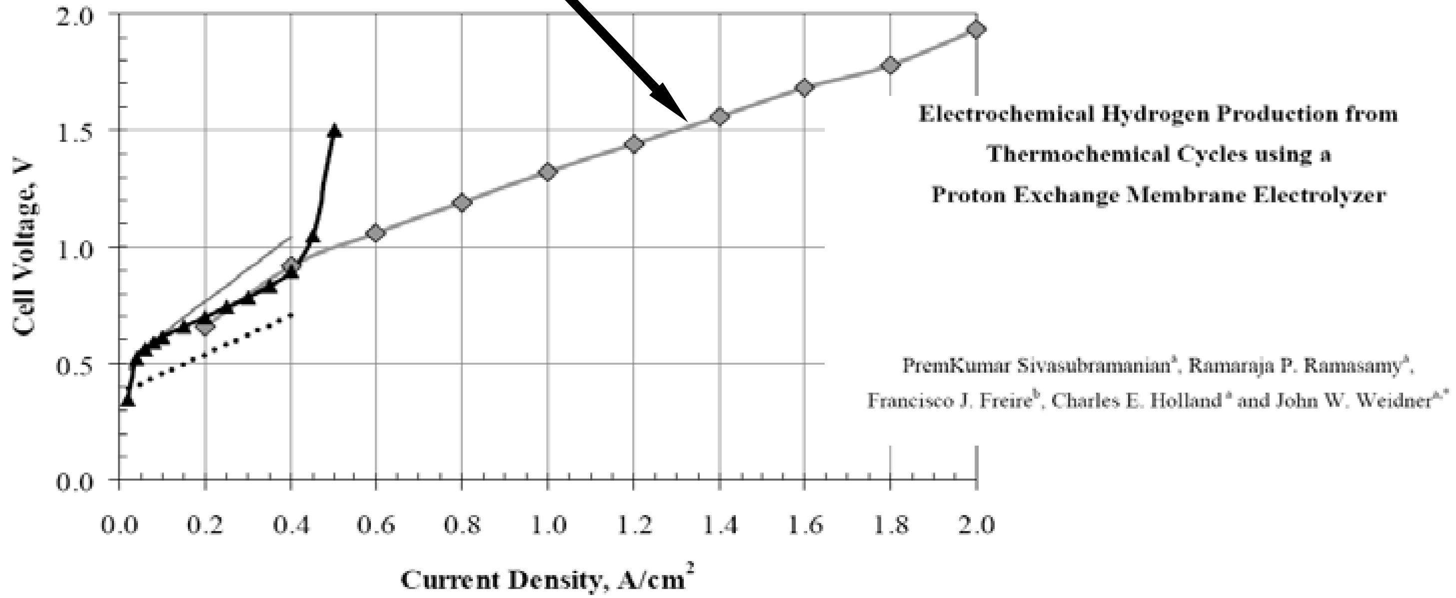


Aspen Plus 11.1 Run:PSA 2003-09-13a 9/13/2003 9:42:00 AM

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



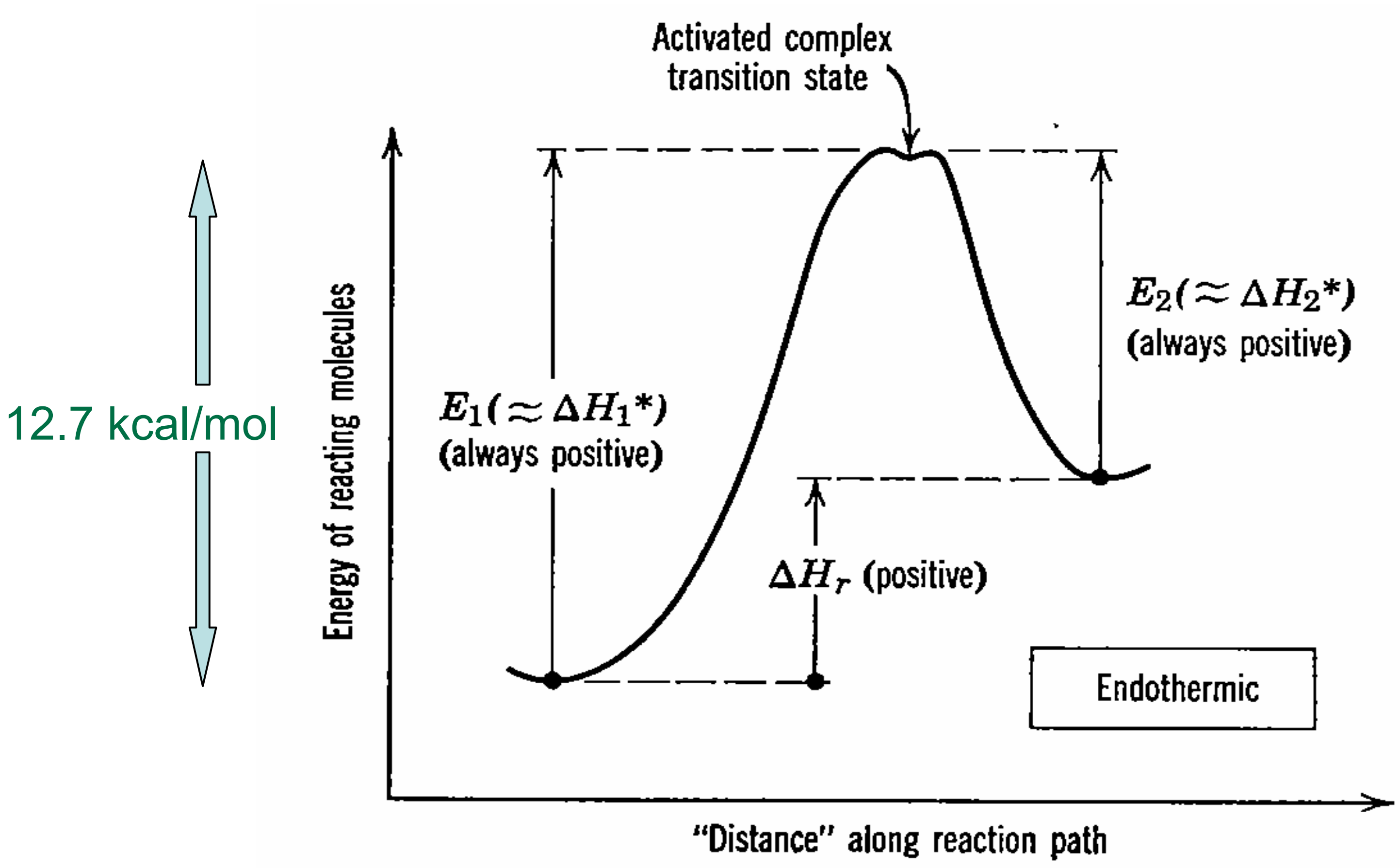


Electrochemical Hydrogen Production from Thermochemical Cycles using a Proton Exchange Membrane Electrolyzer

PremKumar Sivasubramanian[a], Ramaraja P. Ramasamy[a],
Francisco J. Freire[b], Charles E. Holland[a] and John W. Weidner[a,*]

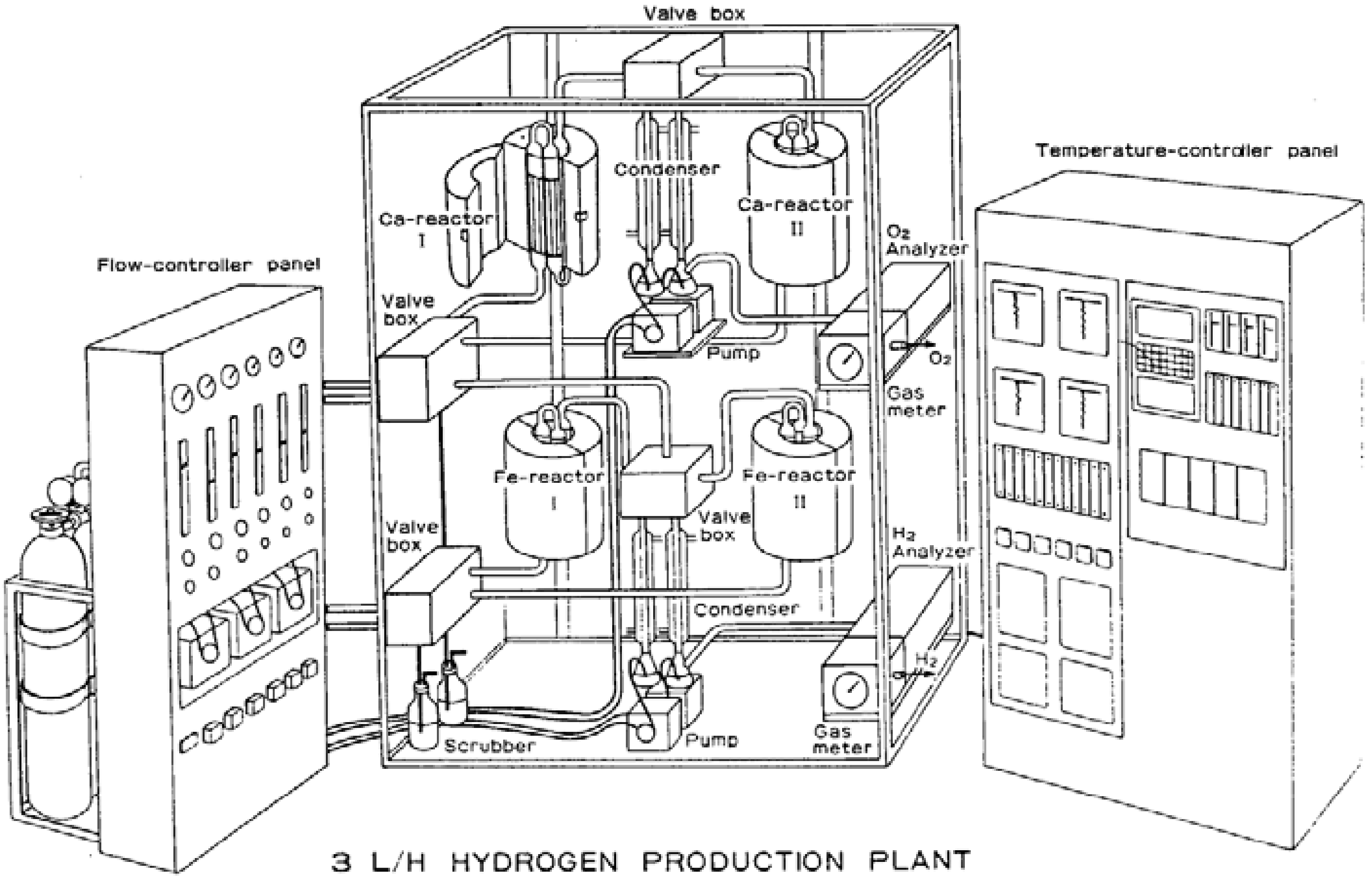
Figure 7: The current-voltage response for SO_2 (▲) and HBr (◆) electrolysis in a PEM electrolyzer. The results for the SO_2 electrolysis are the same as that given in Figure 5 but with a wider voltage scale. The HBr electrolyzer was operated at 80°C, 1.0 atm, and 50% conversion with a RuO_2 loading 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]

188 T. NAKAYAMA *et al.*



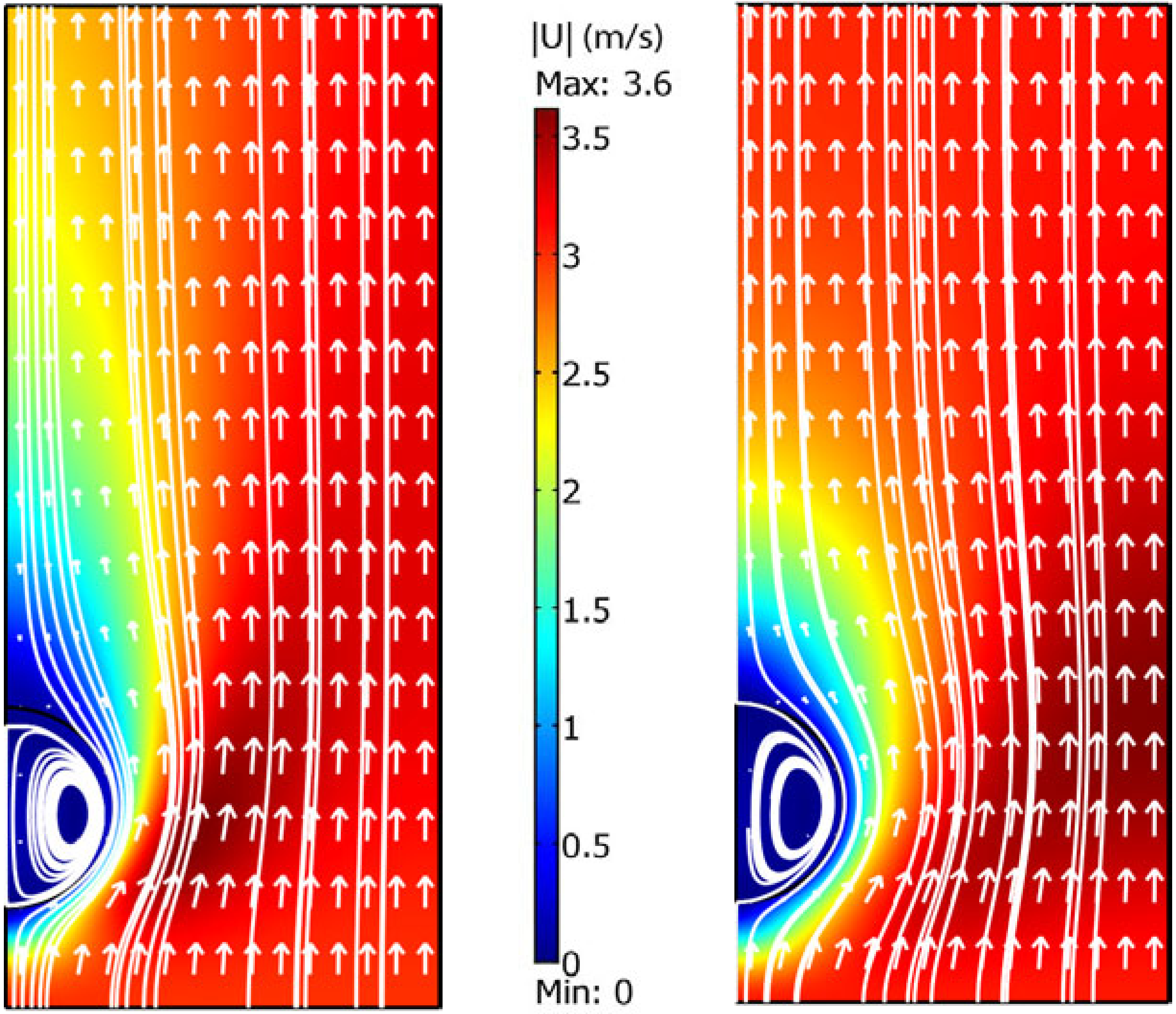
3 L/H HYDROGEN PRODUCTION PLANT

Initial $CaBr_2$ Droplet Model

Inlet velocity

3 m/s 1073 K steam

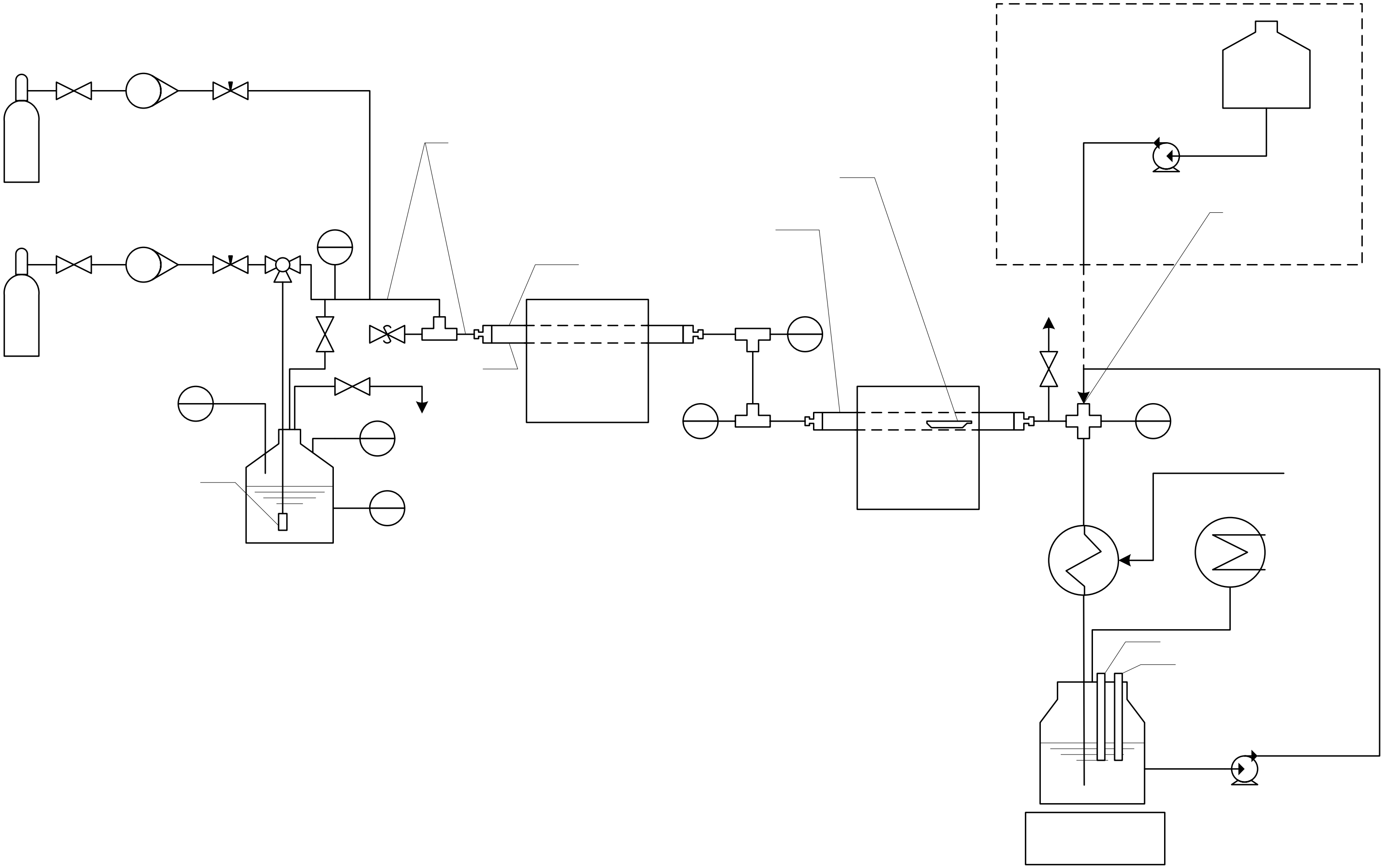
1 mm droplet
Re=15



Color scale is velocity magnitude

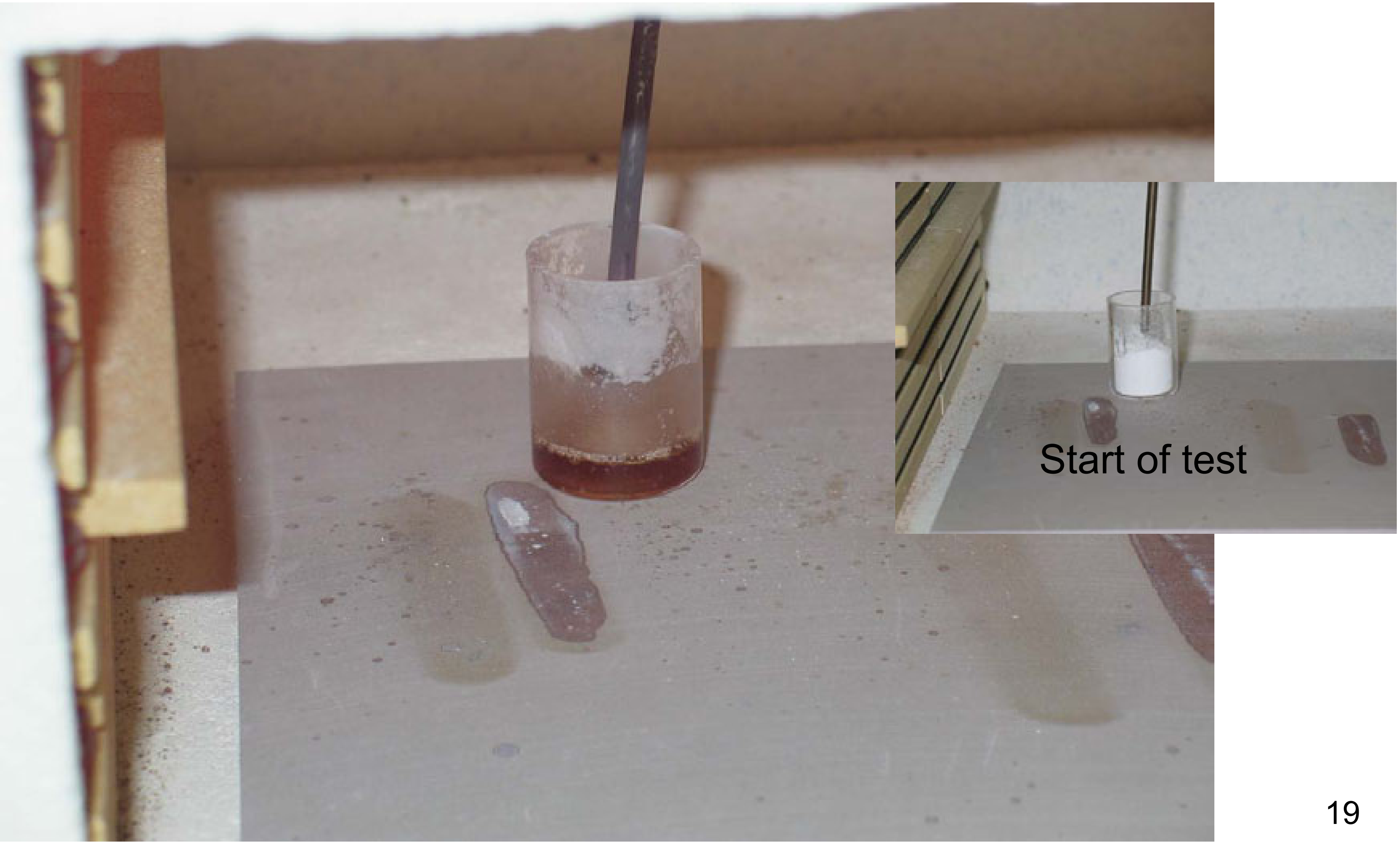
100 µm droplet
Re= 1.5

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



Propo

Anhydrous $CaBr_2$ melting ~780 °C 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			$MW_{Thermal}$			*Efficiency*	$MW_{Electric}$
	T_{IN} (K)	T_{OUT} (K)	*IN*	*BRAYTON*	*REJECT*	*%*	
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

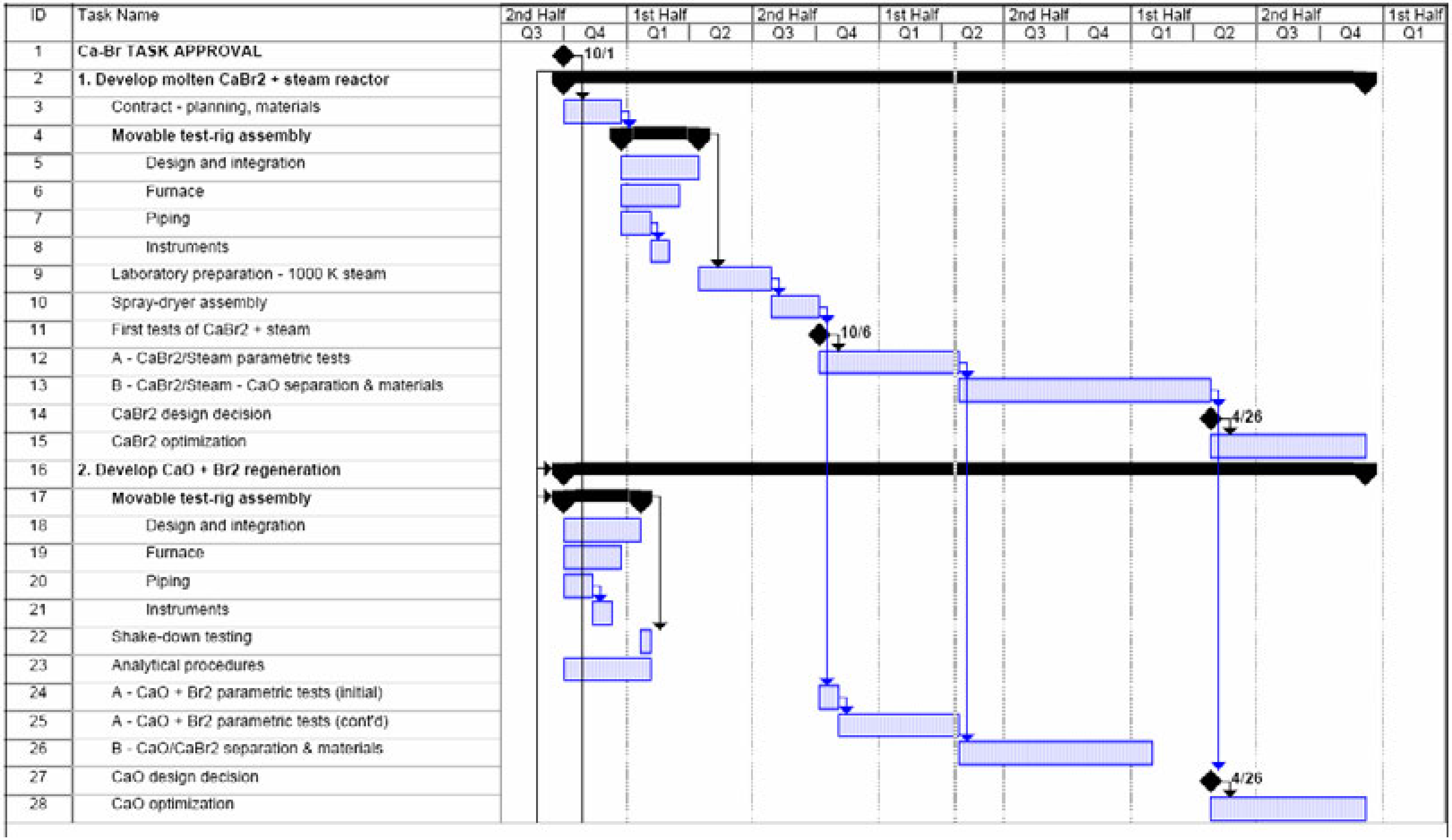
NHI Calcium-Bromine Cycle

- 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

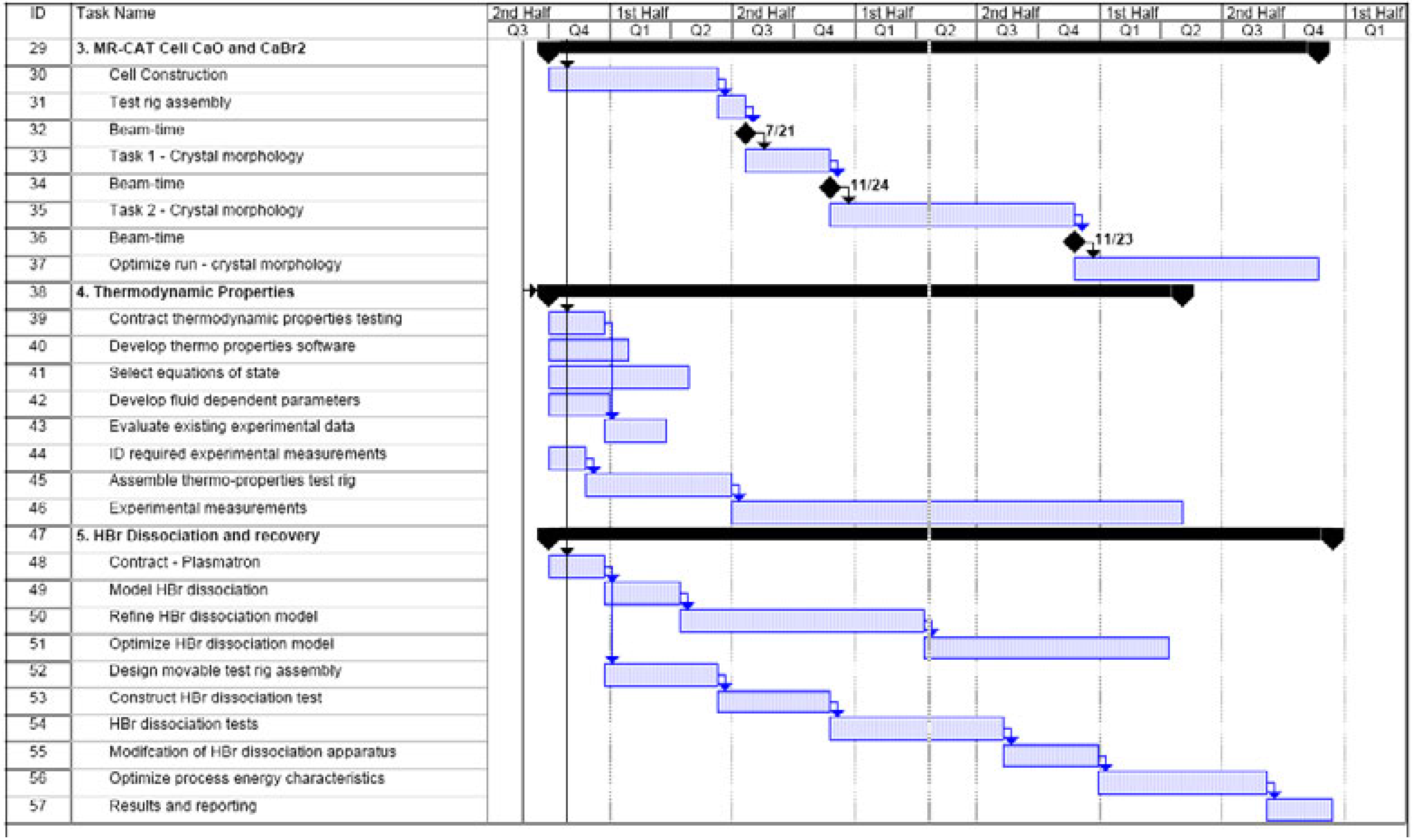
- All project efforts now focus on a continuous process to provide a better opportunity to meet the challenges of kinetics, materials, and operational issues using laboratory experiments
- Two laboratory routes to forming HBr (PEM and non-thermal plasma) are in the testing stage. Both of these show advantages 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



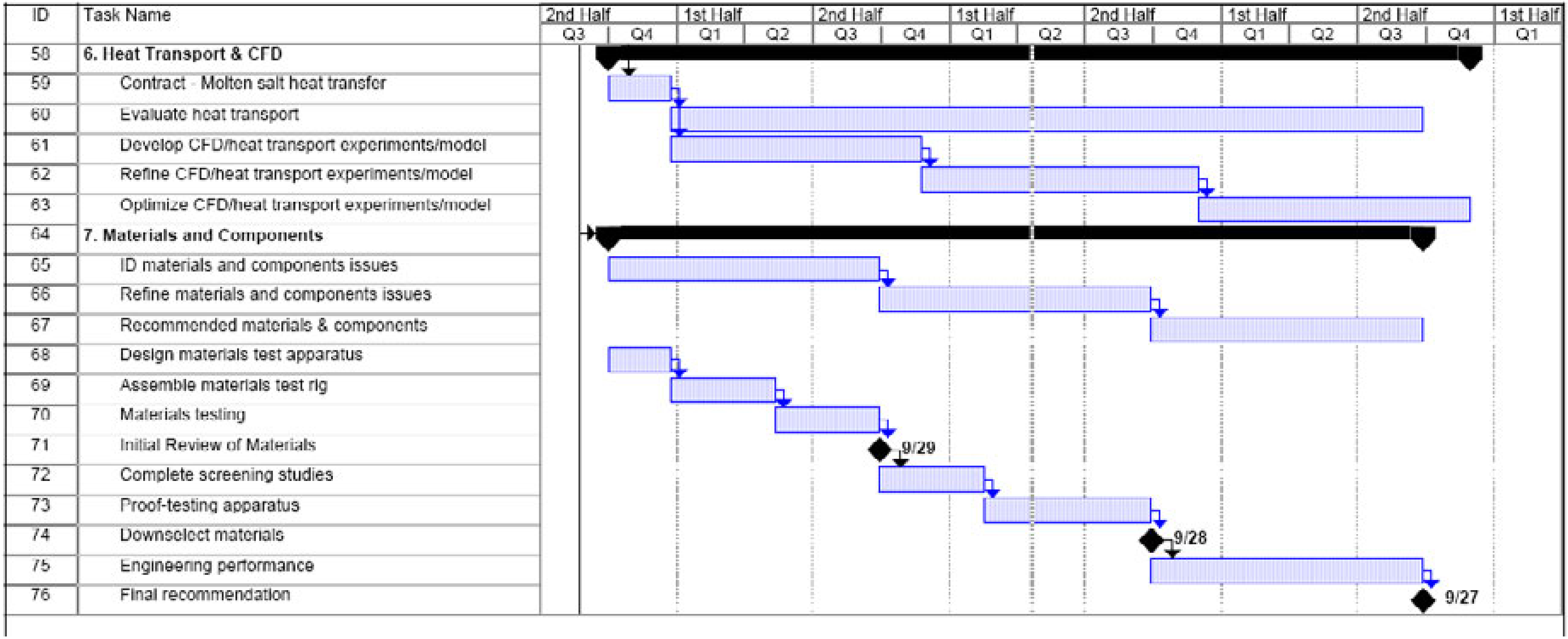
ID	Task Name
1	Ca-Br TASK APPROVAL
2	**1. Develop molten CaBr2 + steam reactor**
3	Contract - planning, materials
4	**Movable test-rig assembly**
5	Design and integration
6	Furnace
7	Piping
8	Instruments
9	Laboratory preparation - 1000 K steam
10	Spray-dryer assembly
11	First tests of CaBr2 + steam
12	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



ID	Task Name
29	**3. MR-CAT Cell CaO and CaBr2**
30	Cell Construction
31	Test rig assembly
32	Beam-time
33	Task 1 - Crystal morphology
34	Beam-time
35	Task 2 - Crystal morphology
36	Beam-time
37	Optimize run - crystal morphology
38	**4. Thermodynamic Properties**
39	Contract thermodynamic properties testing
40	Develop thermo properties software
41	Select equations of state
42	Develop fluid dependent parameters
43	Evaluate existing experimental data
44	ID required experimental measurements
45	Assemble thermo-properties test rig
46	Experimental measurements
47	**5. HBr Dissociation and recovery**
48	Contract - Plasmatron
49	Model HBr dissociation
50	Refine HBr dissociation model
51	Optimize HBr dissociation model
52	Design movable test rig assembly
53	Construct HBr dissociation test
54	HBr dissociation tests
55	Modifcation of HBr dissociation apparatus
56	Optimize process energy characteristics
57	Results and reporting

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).