DOE/GO/10170--T10

Process Study:

Analysis of the HBr-based Hydrogen Production Process

as being developed by

The SRT Group, Inc.

Prepared by:

J. Philip DiPietro
Edward G. Skolnik

Energetics, Incorporated

Prepared for:

Sentech, Incorporated
Under
Subcontract Number 96DE-GFO01-EN1003
Prime Contract Number DE-FC36-96GO10170

October, 1997

Analysis of the HBr-based Hydrogen Production Process being developed by the SRT Group Inc.

Executive Summary

The SRT Group is developing a process that produces hydrogen from the electrolysis of hydrobromic acid. Compared to conventional water electrolysis, HBr electrolysis requires about 25% less electricity per unit of hydrogen produced. The capital and O&M costs are higher though, because of equipment that is required to regenerate HBr from the bromine formed in the electrolyzer (as a comparison a water electrolyzer discards the oxygen product and imports new water feedstock). Exhibit 1 presents summary statistics for the HBr and water electrolysis systems. All else equal, the HBr electrolysis process will be favorable to water electrolysis in situations where electricity is more expensive. A cost model is developed for water and HBr electrolysis systems. It indicates that HBr electrolysis is favored when the average cost of electricity exceeds 5.9 cents/kWh , at which price the cost of hydrogen is 2.8 $/kg (20 $/MMBtu). In most cases steam methane reforming would be preferred if electricity costs are higher than 4 cents/kWh, indicating little commercial viability for HBr electrolysis. The cost of operating the HBr production system and the required safety and control systems for a unit placed at an industrial facility are areas of significant uncertainty for the HBr electrolysis system. Our base case assumptions are aggressively low.

Exhibit 1. Key Results for Water and HBr electrolysis systems*

	Water Electrolysis	HBr Electrolysis
Installed Capital Cost, $	515,000	669,000
O&M cost, $/yr	15,500	63,100
Electricity consumption, kWh AC / kg H_2	0.09	0.06
Natural gas consumption, MMBtu/kg H_2	---	0.11

* Data based on a system with a capacity of 23.5 kg/hr of hydrogen

October, 1997

Background

In 1994 and 1995, SRT Group initiated the development of a solar-based hydrogen production process. The process used solar thermal energy to produce hydrobromic acid (HBr) from bromine and water {1}. The hydrobromic acid was then electrolyzed to form hydrogen and bromine {2}.

$Br_2 + H_2O \text{ --> } 2\ HBr + ½\ O_2$ 16.5 kcal $_{heat}$ /mole HBr {1}

$2\ HBr \text{ --> } H_2 + Br_2$ 0.06 kWh $_{electric}$ / mole H_2 {2}

An analysis conducted by Energetics Inc. showed that the solar-based hydrogen production process was not economically viable [Engineering and Economic Analysis of Solar Reactor Technology's Solar-driven Hydrogen Production Process, 6/28/96]. The primary problem is that reaction {1} has a low equilibrium conversion rate, 10% at 1,000 C. Moreover, the separation process required condensing all the unreacted bromine and water to remove oxygen from the system. A large amount of carrier fluid was heated to 1,000C and then cooled back down to 100 C requiring a large solar thermal input and large heat exchangers (the sensible heat requirement was three times the heat required to drive the primary reaction). Finally, the high process temperature and corrosiveness of the bromine and hydrobromic acid required expensive materials of construction and safety systems.

In 1996, SRT Group proposed a revised concept that addressed the issues associated with the solar-based process. Their idea is to add methane to the reactor with the bromine and water. The methane scavenges the oxygen produced in reaction {1} thus driving a higher conversion of bromine to HBr. Also, the reaction of methane and oxygen provides needed heat. The SRT Group has tested this concept in the laboratory and has demonstrated hydrogen production. The purpose of this analysis is to assess the economic potential of SRT Group's innovation.

Description and characterization of the revised HBr electrolysis process

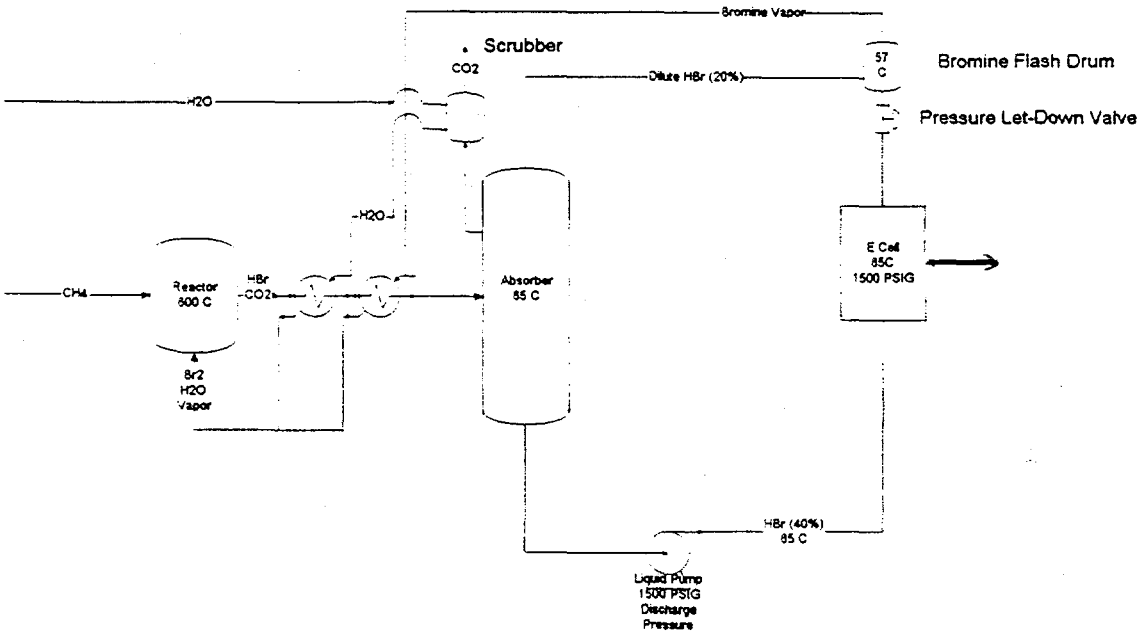
Exhibit 2 is a process flow diagram of the SRT Group's concept. A mixture of bromine, water, and natural gas is heated to 600 C and charged to a reactor. In the reactor bromine is converted to hydrobromic acid through the following overall reaction:

$4\ Br_2 + 2\ H_2O + CH_4 \text{ --> } 8\ HBr + CO_2$ {3}

Heat is recovered from the reaction products and then they are charged to an absorber where the gaseous effluent is contacted with dilute HBr solution. The HBr and bromine are absorbed into the dilute acid; vapor overheads containing mostly CO_2 are scrubbed to remove trace bromine and acid and then vented. A concentrated acid stream from the bottom of the absorber is charged to a PEM electrochemical cell where the HBr is dissociated forming bromine and hydrogen gas. The hydrogen gas is formed on the opposite side of the PEM membrane and collected as product.

Hydrogen outlet pressures of up to 1,500 psi can be achieved at low cost by raising the outlet pressure of the concentrated acid pump. A mixture of bromine, water, and residual HBr is removed from the cell and flashed to remove bromine. The bromine vapor from the flash drum is recirculated to the reactor. The liquid from the bottom of the flash drum is a dilute acid which is charged to the absorber.

Exhibit 2. Process Flow Diagram of the HBr electrolysis process



In analyzing the process, we first seek to develop a heat and material balance. Unfortunately, difficulties in measuring the flowrates of the various species have delayed SRT Group from producing laboratory data. We have made the following assumptions regarding the reactor performance. These assumptions are consistent with the qualitative results produced from the SRT Group thus far and will be replaced with laboratory data when it is available.

- Stoichiometric amounts of water and bromine are charged to the reactor.
- All of the oxygen reacts with methane.
- 80% of the bromine charged to the reactor is converted to HBr.

- The oxygen reacts with methane to form carbon monoxide. Since the oxygen is consumed as it is produced, the methane is likely not fully combusted. Rather, the partial combustion product, carbon monoxide, reacts with bromine, which is abundant, to form $COBr_2$. The $COBr_2$ then readily reacts with water to form HBr and carbon dioxide.

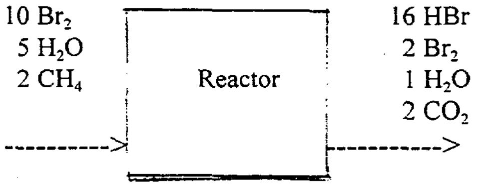
- Methane and water do <u>not</u> react to form hydrogen and carbon monoxide at the reactor temperatures.

The following series of reactions model what goes on in the HBr reactor. The reactions sum to the overall reaction {3}.

$6\ Br_2 + 6\ H_2O \text{ --> } 12\ HBr + 3\ O_2$ {4}
$2\ CH_4 + 3\ O_2 \text{ --> } 2\ CO + 4\ H_2O$ {5}
$2\ CO + 2\ Br_2 \text{ --> } 2\ COBr_2$ {6}
$2\ COBr_2 + 2\ H_2O \text{ --> } 2\ CO_2 + 4\ HBr$ {7}

Exhibit 3 shows the reactor charge and products based on reaction {3} and the above assumptions. The flowrates are arbitrarily normalized to 10 moles of bromine.

Exhibit 3. Molar flows in and out of the bromine reactor



The consumption of natural gas per unit hydrogen produced is calculated as follows:

$$\frac{2 \text{ moles } CH_4}{16 \text{ moles HBr}} * \frac{2 \text{ moles HBr}}{1 \text{ mole } H_2} * \frac{0.000845 \text{ MMBtu NG}}{\text{mole NG}} * \frac{1 \text{ mole } H_2}{0.002 \text{ kg}} = 0.106 \text{ MMBtu NG / kg } H_2$$

As a comparison, a conventional steam methane reformer consumes 0.17 MMBtu NG per kg hydrogen produced. At the base case natural gas cost, 2.3 \$/MMBtu, natural gas feedstock adds 0.244 \$/kg to the cost of hydrogen from HBr electrolysis.

Exhibit 4 lists the pertinent thermodynamic data for the reaction species. Based on the data in Exhibit 4, the heat of reaction {3} is calculated as follows:

$$\begin{aligned} \Delta H_r &= 8 * \Delta H_f HBr + 1 * \Delta H_f CO_2 - [\ 4 * \Delta H_f Br_2 + 2 * \Delta H_f H_2O + 1 * \Delta H_f CH_4\ ] \\ &= -\ 244 \text{ kJ} \\ &= -30.5 \text{ kJ per mole of HBr formed} \end{aligned}$$

The overall reaction is exothermic, and the resulting temperature rise across the reactor is calculated as follows (as a simplified approach we estimate the temperature rise based on the reaction product mixture only):

$$\begin{aligned}\Delta T &= 16 * \Delta Hr / [16*C_pHBr + 2*C_pBr_2 + 1*C_pH_2O + 2*C_pCO_2] \\ &= 16 * 30{,}500 \text{ J} / 734 \text{ J/C} \\ &= 665 \text{ C}\end{aligned}$$

Exhibit 4. Thermodynamic properties of the reactant and product species

Species	C_p Heat capacity (J/moleC)	ΔH_f Heat of Formation (kJ/mole)
Bromine	38	0
Steam	40	-247
Methane	69	-88
Hydrogen bromide	32	-54
Carbon dioxide	53	-394

Properties at 600C, source: CRC Handbook

This is a significant temperature boost and should be enough of a delta to raise the reactor charge from 65 to 600 C. Excess water may be charged to the reactor to absorb some of the heat. Also, in practice, a small amount of excess methane will be charged to the reactor to insure that all the oxygen is consumed. If so the unreacted methane will come off of the scrubber with the CO_2, and could be burned to provide additional charge preheat. The excess methane and the burner equipment are not significant cost drivers and are ignored.

The HBr must be electrolyzed to produce hydrogen. The electricity consumed by an electrochemical cell equals the change in the Gibb's free energy as follows:

$$\Delta G = n * F * \Delta E$$

where:

ΔG - change in Gibb's free energy
n - number of moles of electrons per mole of product
F - the energy content in a mole of electrons
ΔE - the potential difference between the cathode and anode

The theoretical potential required to dissociate HBr is 1.05 V. Commercial electrolyzers are operated at higher rates of current flow, which minimizes the required surface area of electrode per unit of hydrogen produced but also introduces resistive losses that raise the required voltage above the theoretical. We assume that 1.14 volts are required in a commercial electrolyzer. Two moles of electrons are required for each mole of hydrogen generated, and the Faraday constant equals 0.0268 kWh/volt. The energy consumption of an HBr electrolyzer equals:

$$\begin{aligned}\Delta G &= 2 * 0.0268 \text{ kWh/V} * 1.14 \text{ V} \\ &= 0.061 \text{ kWh}_{\text{electric}} / \text{mole } H_2\end{aligned}$$

Including a 2% loss of rectifying grid AC, the electricity consumption increases to 0.062 kWh AC/mole H_2.

Economic Analysis and Cost Models

Because the HBr system has a significant electric input, it is important to demonstrate that it is superior to water electrolysis. The theoretical potential required to dissociate water is 1.229 volts. A typical commercial water electrolyzers operates at 1.5 Volts. By the above equations this gives an electricity consumption of 0.0804 kWh AC/mole H_2, or 0.0194 kWh/mole H_2 more than an HBr electrolyzer. The question is, "Is the additional equipment required to generate HBr from bromine "paid for" by this 25% reduction in electricity consumption?" There are strong economies of scale associated with the bromine reactor and separation processes, so the HBr process does not make sense at small capacities. Also, considering the trouble of starting and shutting down the reactor, the HBr system is better suited for continuous demand applications. We compare the HBr system to 1 MW water electrolyzer that operates 24 hours per day. The time frame for the analysis is the year 2000, and we compare a PEM water electrolyzer to an HBr system using a PEM HBr electrolyzer.

The scenario for the water electrolyzer is as follows. Its rated electric input rate is 1 MW, and it operates at 1.5 volts giving an hydrogen production efficiency of 82%. Its on stream rate is 90%. The capital cost is 500 $/kW which includes 50 $/kW for a water de-ionizer, and 50 $/kW for a rectifier/transformer. The operation and maintenance cost equals 3% of capital or 15,000 $/yr. Installation should be a relatively minor expense and is estimated to be $15,000.

The average cost of electricity is a key input. We use an average electricity cost of 5 cents/kWh for the base case (AEO 97 industrial sector reference case).

Exhibit 5 presents a cash flow analysis of the water electrolysis system. The cost of hydrogen is the independent variable and is adjusted to provide an 11% after-tax internal rate of return (11% IRR is the "standard rate of return used for analyses in the Hydrogen Program). Based on all the inputs described above the cost of hydrogen from the water electrolysis system is 2.5 $/kg (18 $/MMBtu).

Assuming that the water and HBr electrolyzers operate at the same current density, an HBr cell will be more expensive per kW of electric input capacity but the cost will be the same per unit of hydrogen produced. Thus we assume the HBr electrolyzer costs the same as the 1 MW water electrolyzer, $400,000. The power conversion system will be less costly because of the reduced

Exhibit 5. Water eletrolysis hydrogen production

Capacity, electric input, kW	1,000
Cell potential, volts	1.5
Electrolyzer cost, $/kW	400
PCS cost, $/kW	50
De-ionizer cost, $/kW	50
total	500
Efficiency, LHV basis	82%
On-stream factor	90%
Electrolyzer O&M, percent of capital	3%
Installation time, months	3
Annual electricity consumption, kWh	7,884,000
Annual hydrogen production, kg	194,141
Electricity cost, cents/kWh	5
Hydrogen cost, $/kg	2.45
Hydrogen kWh/kg	33.3
Equipment capital cost, $	500,000
Installation	15,000
Total investment	515,000
Annual electricity cost	394,200
Annual O&M	15,450
Total O&M	409,650
Salvage value	10%
Percent of cap that is depreciable	100%
Marginal tax rate	28%

Year	Operating Revenues	Operating Cost	Operating Income	Capital investment	Depreciation	Taxable Income	Taxes	After-tax income	Cash Flow
1	357,418	307,238	50,181	515,000	50,181	-	-	-	(464,819)
2	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
3	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
4	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
5	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
6	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
7	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
8	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
9	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
10	476,558	409,650	66,908		51,500	15,408	4,314	11,094	62,594
11	476,558	409,650	66,908		1,319	65,589	18,365	47,224	48,543
12	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
13	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
14	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
15	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
16	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
17	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
18	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
19	476,558	409,650	66,908		-	66,908	18,734	48,174	48,174
20	476,558	409,650	66,908	(51,500)	-	118,408	33,154	85,254	85,254
				total dep	515,000				

IRR	**10.9%**
H2 cost $/kg	2.45

electricity flow (1.14/1.5)*\$50,000 = \$38,000. A water deionizer is not needed. Assume that O&M and installation costs are the same as for a water electrolyzer 3 percent of capital and \$15,000 respectively.

The hydrogen production rate of the 1 MW water electrolysis system equals

$$\frac{1{,}000 \text{ kWh electric}}{1 \text{ hour}} * \frac{1 \text{ mole } H_2}{.0804 \text{ kWh}} = 12{,}440 \text{ moles } H_2\text{/hr}$$

The HBr-based system will have the same hydrogen production rate. To keep up with the electrochemical cell, the reactor must produce 24,880 moles of HBr per hour. Based on Exhibit 3, for every 16 moles of HBr there are 21 moles of total effluent, giving a reactor flowrate of 30,883 moles/hr. Assuming a 2-second residence time, the reactor must hold 18.2 moles of gas. Assuming the reactor operates at 1.5 atm and 600C, the required reactor volume is estimated using the ideal gas law as follows:

$$\begin{aligned}\text{reactor volume} &= 18.2 \text{ moles} * 873 \text{ K} * 82.05 \text{ cm}^3 \text{ atm/mole K} / 1.5 \text{ atm} \\ &= 0.9 \text{ m}^3\end{aligned}$$

The concentration of HBr solution charged to the electrochemical cell is 40 wt%. The specific gravity of 40 wt% HBr is 1.39 (Perry's 6th edition, p. 3-89). The volumetric flowrate of solution to the cell is calculated as follows.

$$\frac{24{,}880 \text{ moles HBr}}{1 \text{ hour}} * \frac{81 \text{ g HBr}}{1 \text{ mole HBr}} * \frac{1 \text{ g solution}}{0.4 \text{ g HBr}} * \frac{1\text{x } 10\text{-}6 \text{ m}^3}{1.39 \text{ g solution}} = 3.6 \text{ m}^3 \text{ solution / hr (16 gpm)}$$

The required absorber volume is estimated to be 6 m^3.

The reactor charge preheat exchangers must vaporize the water and heat the steam and bromine gas to 600C. As shown in Exhibit 3, every 16 moles of HBr out of the reactor requires 10 moles of bromine charge and 5 moles of steam. Based on an HBr production rate of 24,880 moles, the charge rate of bromine and steam is 15,550 and 7,775 moles/hr respectively. The duty of the exchangers is calculated as follows:

Br_2 15,550 moles Br_2/hr * 38 J/ moleC * (600-65)C * 9.5x10^{-4} Btu/J = 300,000 Btu/hr

H_2O 7,775 moles H_2O/hr * [40 J/moleC * (600-65)C + 43,930 J/mole]* 9.5x10^{-4} Btu/J = 480,000 Btu/hr

The H_2O duty contains the heat required to vaporize water (43,930 J/mole) which represents 2/3 of the water duty. The log mean temperature difference is estimated to be 325C (585 F). Assuming an overall heat transfer coefficient of 20 Btu/hrft^{2}F, the required heat transfer area equals:

$$\text{Exchanger Area} = 780{,}000 \text{ Btu/hr} / 585 \text{ F} / 20 \text{ Btu/hrft}^2\text{F} = 67 \text{ ft}^2$$

Exhibit 6 presents a capital cost estimate for the HBr production component of the HBr electrolysis system. The costs of each component is estimated from the information calculated above. This is a preliminary estimate; a more detailed assessment could identify safety/control equipment that could increase the capital cost substantially. Note, we assume the scrubber will be sized to be able to knock down any vapors resulting from a process upset. It will be much larger than what is required for normal operation.

Exhibit 6. Capital cost estimate for the HBr production system
(1996$)

Reactor, quartz, 0.9 m^3	10,000
Exchangers, ceramic tubes, 67 ft^2	15,000
Absorber, packed tower, glass lined steel, 6 m^3	60,000
Concentrated acid pump, 16 gpm	3,000
Pressure let down valve	1,000
Bromine flash drum	5,000
Scrubber	15,000
Piping	15,000
Controls	20,000
Subtotal	144,000
Installation (50%)	72,000
Total installed capital cost	**216,000**

A large area of uncertainty lies in the operations cost for the reactor and separator system. The annual electrolyzer O&M, 15,000 $/yr, assumes that the unit requires little attention during normal operation. For the HBr production system, the high temperatures of the reactor, the corrosive nature of the chemicals involved, and the exothermic characteristic of the overall reaction all point to human monitoring. Based on an operation labor cost of 50 $/hr, one operator around the clock would cost $450,000 per year. The process is not viable with that cost. The base case estimate for total O&M of $50,000 per year is based on a highly automated system. Demonstrating automated operation is a challenge with a high degree of technical risk. Another way to lower the cost of operation per unit of hydrogen produced is to build a bigger unit, but at larger sizes steam methane reforming becomes competitive.

Exhibit 7 presents a cash flow analysis of the HBr electrolysis process. The HBr model uses the same cost of electricity and the same financial assumptions that are used for the water electrolysis case. The following observations can be made by comparing the cost models for the water and HBr electrolysis systems.

> Because the HBr electrolysis process uses less electricity per unit of hydrogen produced, it has an advantage over water electrolysis in situations where electricity is expensive. Exhibit 8 shows the cost of hydrogen from water and HBr electrolysis over a range of electricity costs under the base case assumptions regarding capital and O&M costs. The break-even electricity price is 5.9 cents per kWh. At electricity costs below that, one is better off with alkaline electrolysis.
>
> The break-even electricity costs is unfortunately high for the HBr process, at electricity costs above 3-4 cents/kWh, steam reforming of natural gas becomes attractive. This is compounded by the fact that the HBr electrolysis system uses natural gas and so is only applicable where natural gas is available. At an electricity cost of 5.9 cents/kWh the cost of hydrogen from electrolysis is 2.8 $/kg (20 $/MMBtu), well above the cost from steam methane reforming.
>
> If the capital cost estimate and the O&M estimate for the HBr production component is reduced by 50%, the break-even electricity price for the HBr electrolysis process is reduced to 4 cents/kWh.

Exhbit 8. Hydrogen Production Cost from Water and HBr Electrolysis

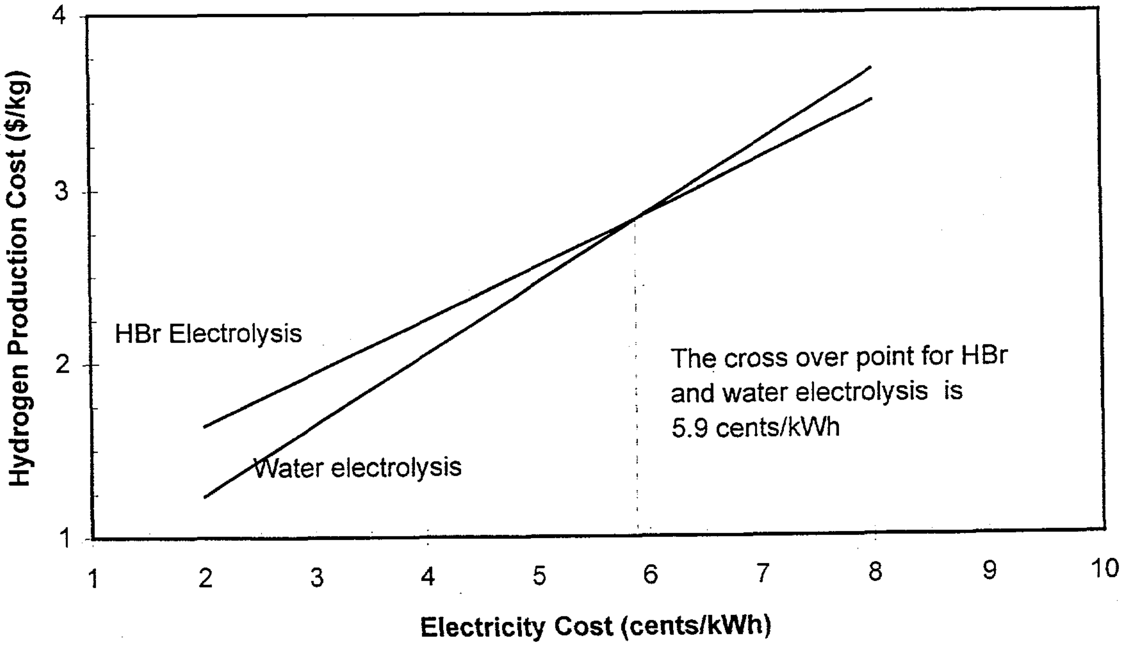


Exhibit 7. HBr eletrolysis hydrogen production

Capacity, electric input, kW	760
Cell voltage	1.14
PCS cost, $/kW	50
Electrolyzer cost, $	400,000
PCS cost, $	38,000
HBr reactor & seperator, $	144,000
Electrolyzer installation	15,000
HBr reactor & seperator intall, $	72,000
Total capital	669,000
On-stream factor	90%
Annual electricity consumption, kWh	5,991,840
Annual hydrogen production, kg	194,141
Electrolyzer O&M, percent of capital	3%
Installation time, months	3
Hydrogen kWh/kg	33.3
Electricity cost, cents/kWh	5
Hydrogen cost, $/kg	2.56
Natural gas cons, MMBtu/kg H2	0.106
Natural gas cost, $/MMBtu	2.3
Annual electricity cost, $/yr	299,592
Natural gas cost, $/yr	47,331
Annual Electrolyzer O&M, $/yr	13,140
Annual HBr reactor O&M, $/yr	50,000
Total	410,063
Salvage value	10%
Percent of cap that is depreciable	100%
Marginal tax rate	28%

Year	Operating Revenues	Operating Cost	Operating Income	Capital investment	Depreciation	Taxable Income	Taxes	After-tax income	Cash Flow
1	373,086	307,548	65,539	669,000	65,539	-	-	-	(603,461)
2	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
3	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
4	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
5	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
6	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
7	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
8	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
9	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
10	497,448	410,063	87,385		66,900	20,485	5,736	14,749	81,649
11	497,448	410,063	87,385		1,361	86,023	24,086	61,937	63,298
12	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
13	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
14	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
15	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
16	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
17	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
18	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
19	497,448	410,063	87,385		-	87,385	24,468	62,917	62,917
20	497,448	410,063	87,385	(66,900)	-	154,285	43,200	111,085	111,085
				total dep	669,000				

IRR	**11.0%**
H2 cost $/kg	2.56