Canadian Advances in Thermochemical H₂ Production in the Context of Conventional Electrolysis



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Outline

The market for hydrogen

SMR vs LTE

The GIF context

AECL work on sulphur thermochemical cycles

Collaboration with USDOE on copper chloride cycles

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Where will the demand be?

- Fuel for road vehicles?
 - Later perhaps but uncertain
 - Depends on battery vs fuel cell development
- More likely for larger vehicles (trains, ships)
- Big market is for upgrading petroleum
 - Exists and is growing rapidly
 - Especially in the oil sands developments in northern Alberta
 - Needs 3 to 5 kg H_2 /bbl
 - Expect over
 2 million bbl/d by 2015
 - 1 GWe = 160 000 bbl/d



How will H₂ be made?

- Conventionally come from natural gas by SMR
 - Cost has risen fast
 - Realistic to base on oil:gas at 6:1
 - Add 70 \$/t CO₂
 - Add 3% leakage of CH₄ from well to end use
 - Supply of natural gas is uncertain
 - All Mackenzie pipeline output could go to oil sands upgrading
- Need a new way
 - High-temperature thermochemical?
 - High-temperature electrolysis?
 - Conventional low-temperature electrolysis?



LTE will be available much sooner

- Make it using Generation III+ reactors
 - Could be deployed by 2015
- Key is to produce H₂ with off-peak electricity
 - Preferably with variablecurrent cells
 - Needs large-scale storage
 - In salt caverns
 - \Rightarrow Alberta case
 - 550 \$/kW cells
 - 5000 \$/t storage
 - Applying real-time Alberta power prices







Intermittent H₂ Production



And later? Within the GenIV, Canada focuses on SCWR with crosslink to VHTR

- Acronym
- SFR Sodium Cooled Fast Reactor
- LFR Lead Alloy Cooled Reactor
- GFR Gas Cooled Fast Reactor
- VHTR Very High Temperature Reactor
- SCWR Supercritical Water Cooled Reactor
- MSR Molten Salt Reactor



Spectrum Fuel cycle

Fast	Closed
Fast	Closed
Fast	Closed
Thermal	Once-through
Th. & F.	Once-t. & Closed
Thermal	Closed



CANDU SCWR Concept

- Started in 1994 as Candu X Program
- Establish the design limits and ultimate potential
- Main CANDU features are retained.
 - Horizontal modular channels.
 - Heavy water moderator.
- Supercritical light water coolant (higher efficiency).
- Advanced fuel channel design (internal insulation without calandria tube).
- Options systematically studied
 - Mark 1: indirect cycle $T_{out} \sim 400^+ \circ C$ set by existing Zr
 - Mark 2: direct cycle T_{out} ~ 600⁺ °C set by existing turbine
 - Mark3: multiple cycle T_{out} >850 + °C set by known materials





The H₂SO₄ Side of I/S and other S Cycles

- $H_2SO_4 \rightarrow SO_3 + H_2O$
 - Majority of energy; lower temperature (< 500°C)
- $SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$
 - Minority of energy; higher temperature (> 700°C)
 - Could avoid a high temperature reactor by providing direct electric heating of a substrate on which catalyst deposited
 - Work so far on selecting catalysts



Assessing catalysts for SO₂ decomp.





A metal (textured Inconel 800) sheet coated with catalyst for SO₃ decomposition



Copper chloride cycles

- Work led by USDOE at Argonne (Michelle Lewis)
- AECL is currently focused on the electrochemical step

#	Reaction Stoichiometry	Temperature (°C)	
1	$2Cu + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$	425-450	
2	$4CuCl(s) \rightarrow 2CuCl_2(a) + 2Cu$	<100	
3	$\begin{array}{r} 2\mathrm{CuCl}_2(\mathrm{s}) + \mathrm{H}_2\mathrm{O}(\mathrm{g}) \rightarrow \mathrm{Cu}_2\mathrm{OCl}_2 \ (\mathrm{s}) + \\ 2\mathrm{HCl}(\mathrm{g}) \end{array}$	300-375	
4	$\operatorname{Cu}_2\operatorname{OCl}_2(s) \to 2\operatorname{CuCl}(1) + \frac{1}{2}\operatorname{O}_2(g)$	450-530	

- Or a variant on reaction #2: $2 \text{ CuCl} + 2 \text{ HCl} \rightarrow 2 \text{ CuCl}_2 + \text{H}_2$
 - Avoids solid phase
 - Preliminary testing yields H_2 from both reactions at ~ 0.65 V

Placing Canada in Global Context



