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# 2023 NETL Multiphase Flow Science Workshop

A fluidized bed approach for hydrogen production from natural gas  
using hot slag from steel plants

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# Background

- The high-quality slag heat is usually lost or downgraded.
- Typically, the intention has been to capture the slag energy as high-temperature air (at 500-600 °C) for use in the plant.
- Climate change concerns have spurred interest in low-carbon fuels and feedstocks.
- Hydrogen is carbon-free, but it needs to be produced.
- A production pathway that has gained attention recently is to decompose natural gas (which consists mostly of methane) into gaseous hydrogen (or a hydrogen-rich gas) and a solid carbon (or carbon-rich) by-product.

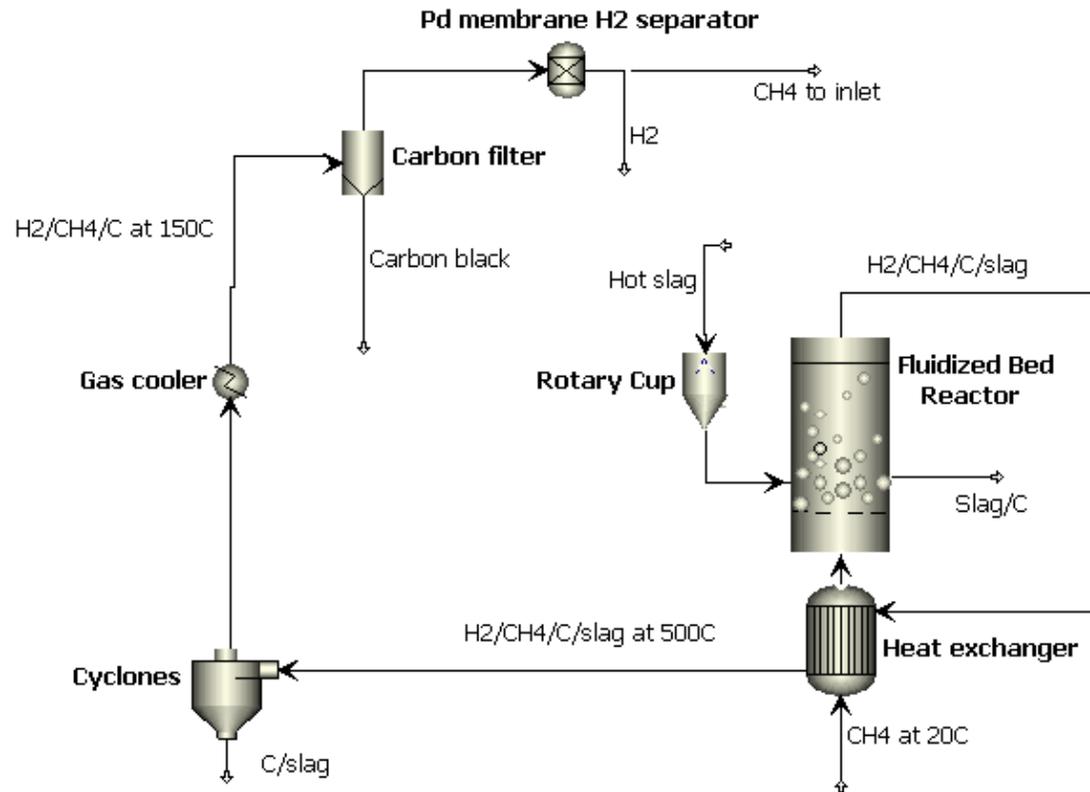


# Natural gas decarbonization

- Essentially,  $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$
- Advantages:
  - The carbon by-product is potentially easier to store or utilize compared to  $\text{CO}_2$ .
  - Possibly more suitable for smaller-scale production than steam-methane reforming.
- Disadvantage:
  - Compared to steam-methane reforming ( $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ ), it produces half the hydrogen per unit methane.
- About 60% of the chemical energy of the methane is retained after decarbonization.
- Proposition: Dry-granulate the slag and use its heat to drive the endothermic methane decomposition, using a fluidized bed to provide contact between slag and natural gas. (“Waste heat to hydrogen”)



# Proposed process



- Performed Aspen Plus process analysis, with blast furnace slag information from a Canadian steel maker.
- Concluded about 20% of the reductant could be replaced by the produced hydrogen. This percentage would depend on the steel-to-slag ratio of a given process.
- Slag flow is not continuous. The slag transfer to the proposed process would need to have buffer capacity for it to operate continuously.

# Operating conditions

We assumed that 80% of the carbon black would deposit on the slag, with the rest entrained by the product gas stream.

Slag input, tonnes/year	367000
Slag input temperature, °C	1300
Natural gas input, tonnes/year	45000
Natural gas temperature, °C	20
Hydrogen produced, tonnes/year	9354
Carbon black produced, tonnes/year	4814
Slag plus deposited carbon black, tonnes/year	389450



# Techno-economic analysis

- The cost of hydrogen production by thermal decomposition of methane using a fluidized bed reactor has been studied in the literature.
- The main difference between the present process and those of the literature is that the thermal energy for this decomposition process comes from the hot slag rather than from burning a portion of the natural gas. However, the required equipment is similar.
- Capital costs from the literature were scaled by equipment capacity, then converted to annual cost using standard capital recovery factor, assuming 10% interest rate and a 15-year investment period.
- Assumed operation and maintenance cost of 2% of the annual capital cost, except for the membrane separator (4%).
- Electricity and fuel costs were included.
- 50% contingency was added.
- The sale price for slag that is uncontaminated by carbon (and therefore useful for cement production) is CAD 25/tonne, whereas for slag that is contaminated by carbon (and therefore only useful as aggregate) it is CAD 5/tonne.
  - Throughout this analysis, we assumed all the slag would be contaminated by carbon.



# Sensitivity to natural gas purchase price and carbon black sale price

Hydrogen production cost estimate at different natural gas purchase prices, with fixed carbon black sale price

Variable	Unit	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Natural gas price	CAD/kg	0.086	0.176	0.320	0.417	0.528	0.632
Natural gas annual cost	CAD Million	3.87	7.92	14.41	18.78	23.78	28.42
Carbon black price	CAD/kg	0.35	0.35	0.35	0.35	0.35	0.35
Slag & carbon black annual sale	CAD Million	3.63	3.63	3.63	3.63	3.63	3.63
Net H <sub>2</sub> annual production cost	CAD Million	5.82	9.86	16.36	20.73	25.72	30.37
Net H <sub>2</sub> cost per kilogram	CAD/kg	0.622	1.055	1.749	2.216	2.750	3.247

Hydrogen production cost estimate at different carbon black sale prices, with fixed natural gas purchase price

Variable	Unit	Case 1	Case 2	Case 3	Case 4
Natural gas price	CAD/kg	0.239	0.239	0.239	0.239
Natural gas annual cost	CAD Million	10.74	10.74	10.74	10.74
Carbon black price	CAD/kg	0.000	0.250	0.500	0.700
Slag & carbon black annual sale	CAD Million	1.95	3.15	4.35	5.32
Net H <sub>2</sub> annual production cost	CAD Million	14.38	13.17	11.97	11.01
Net H <sub>2</sub> cost per kilogram	CAD/kg	1.537	1.408	1.280	1.177

Hydrogen production cost is driven strongly by the purchase price of natural gas, and less strongly by the sale price of carbon black.



# Hydrogen production cost compared to that of other processes

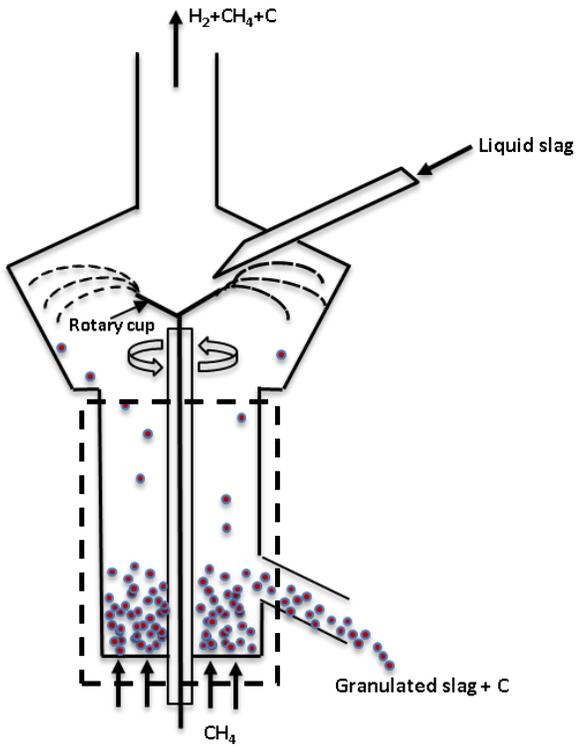
Hydrogen production cost of this process (bold type) compared to those of thermal decomposition of methane (TDM) in which a portion of the natural gas is burned, steam-methane reforming (SMR), and water electrolysis. SS is small-scale, LS is large-scale, and CCS refers to integrated CO<sub>2</sub> capture and storage.

	<b>Slag-TDM</b>	TDM-SS	SMR-SS	SMR-LS	SMR-LS+CCS	Water electrolysis
H <sub>2</sub> production, tonnes/year	<b>9354</b>	529	529	52900	52900	529
H <sub>2</sub> production cost with CO <sub>2</sub> cost, CAD/kg H <sub>2</sub>	<b>2.80</b>	3.88	6.00	2.49	3.25	3.93
H <sub>2</sub> production cost without CO <sub>2</sub> cost, CAD/kg H <sub>2</sub>	<b>2.80</b>	3.86	5.80	2.31	3.17	3.93

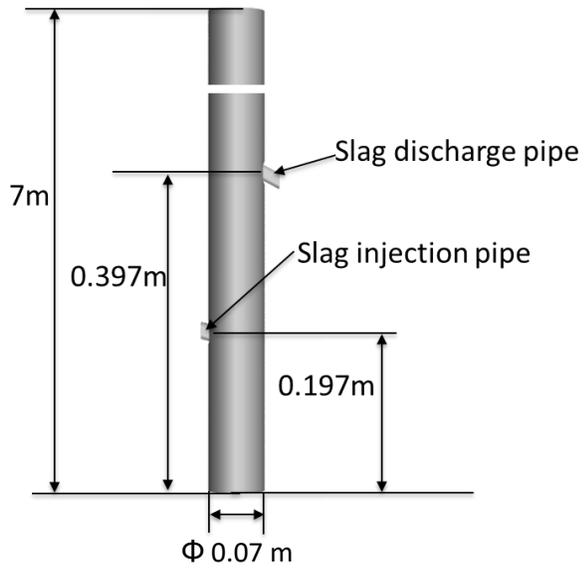
- The proposed process is competitive with large-scale steam-methane reforming with integrated CCS and much less costly than small-scale steam-methane reforming, making it suitable for on-site hydrogen production at a plant, for use in the plant.
- Using the hot slag to drive the methane decomposition reduces hydrogen production cost by 25% compared to combusting a portion of the natural gas itself.

# Technical Assessment of Reactor Concept

Schematic



Pilot-scale fluidized bed geometry



Operating conditions

Solids holdup	7.9 kg
Overall bed pressure-drop	0.2 bar
Bed temperature	1083 °C
CH <sub>4</sub> injection rate	1.5 kg/h
CH <sub>4</sub> injection temperature	500 °C
Slag injection rate	37.8 kg/h
Slag injection temperature	1300 °C

# Technical Assessment of Reactor Concept

- Reaction:  $CH_4 + C_{core} \rightarrow (C_{core} + C) + 2 H_2$ , where  $C_{core}$  represents nucleation particles of carbon-black-size but with very small mass
- Used the dense discrete phase model in ANSYS-Fluent
- Particle-particle interactions were modelled using the kinetic theory of granular flow.
- Three discrete phases: slag particles initially in the bed, injected slag particles, and carbon particles
- Preliminary simulations indicated that particles with diameter less than 140  $\mu\text{m}$  would likely be blown out of the bed. Accordingly, the slag bed and injected slag consisted of particles with diameters of 150, 210, 270, 330 and 390  $\mu\text{m}$ , evenly distributed.
- Carbon particle diameters ranged from 0.2  $\mu\text{m}$  to 3  $\mu\text{m}$  with mean diameter of 1  $\mu\text{m}$  and spread factor of 3.1, according to carbon black samples measured by CanmetENERGY-Ottawa. Carbon was then added to these particles as the methane decomposed and, as the carbon deposited, the particle diameters remained constant while the particle densities increased.



# Technical Assessment of Reactor Concept

- P1 radiation model was used to model the radiation heat transfer and the weighted-sum-of-gray-gases model was used for the absorption coefficient of the gas phase.
- The particles participated in the heat transfer by convection, radiation, and, in the case of the carbon particles, an endothermic methane-decomposition surface reaction.

Particle heat transfer parameters

Slag particle heat capacity, $J/(kg \cdot K)$	960
Carbon particle heat capacity, $J/(kg \cdot K)$	1680
Endothermic heat of methane decomposition, $kJ/mol_{CH_4}$	76
Fraction of endothermic reaction heat taken from particle (remainder taken from gas phase)	0.3
Radiative surface emissivity of slag particles	0.9
Radiative surface emissivity of carbon particles	0.9

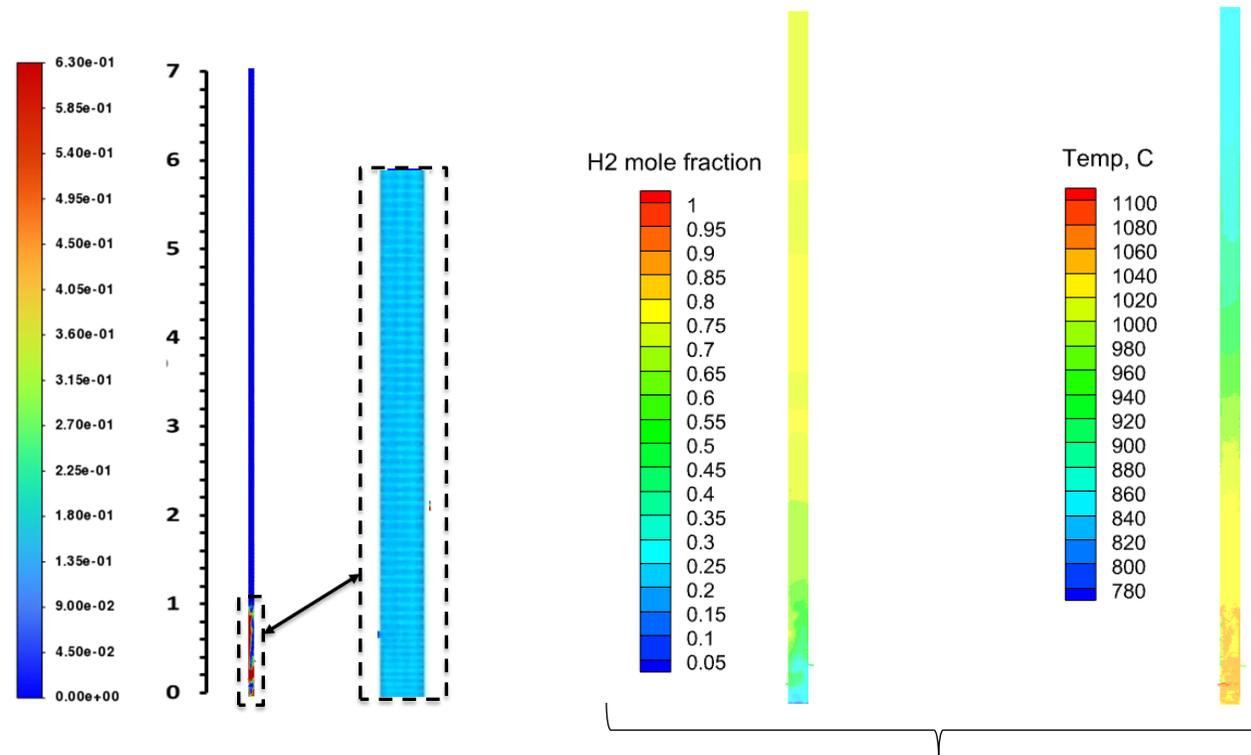


# Technical Assessment of Reactor Concept

- CFD model simulated 16 seconds of operation time and achieved steady state with respect to fluidization and methane decomposition.
- The relatively short, simulated operation time, due to the computational intensity, meant that the simulation could not achieve steady state with respect to solids inventory in the bed. It was, therefore, decided to not allow solids to exit the reactor through the discharge pipe.
- Hot slag particles entered through the injection location to compensate for heat consumed by methane decarbonization. As a result, the bed solids inventory increased by 2% during the 16 seconds.



# Technical analysis results



The 7-meter reactor height has been compressed by half in these plots.



# Technical analysis results

- Average, steady state bed temperature remained between 1020 and 1060 °C.
- Average temperature of the gases exiting the reactor was 850 °C.
- In the configuration studied here, the resulting mole fraction of hydrogen depended significantly on the decomposition reaction kinetics employed.
  - Using one set of kinetics from the literature, the hydrogen mole fraction was 0.7. This implies a 53.8% conversion of methane to hydrogen (each mole of converted methane results in two moles of hydrogen).
  - Using another set of kinetics from the literature, the hydrogen mole fraction was 0.9. This implies an 82% methane conversion.
- The sensitivity to reaction kinetics is not unexpected, given that the decomposition of methane is influenced by catalytic effects that depend on the composition of the material in contact with it, particularly when the material contains metal compounds.



# Conclusion

- It is expected that about 20% of the reductant could be replaced by the produced hydrogen, depending on the steel-to-slag ratio of a given process.
- A techno-economic analysis was performed, suggesting that the proposed hydrogen production process would be competitive with large-scale steam-methane reforming with integrated CCS and much less costly than small-scale steam-methane reforming, making it suitable for on-site hydrogen production for use within the plant.
- In addition, using the hot slag to drive the methane decomposition would reduce hydrogen production cost by 25% compared to combusting a portion of the natural gas itself.
- A CFD analysis suggested that the fluidized bed approach is an appropriate method to provide methane-slag contact and decarbonization of methane. It operated in the bubbling bed regime.
- Further work would be required to optimize the design and operation, and to control the solids inventory in the fluidized bed. Further (likely experimental) investigations would be required to reduce the uncertainty of the chemical kinetic rate for methane decomposition as well as to determine the fate of the produced carbon.



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