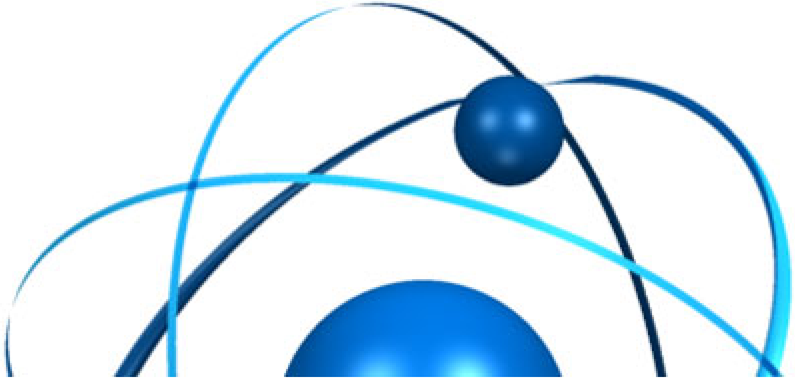

Hydrogen Sensors

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- Sensor capability wish list
- Overview of hydrogen sensor types
  - Existing sensor types
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- HSL hydrogen sensors
  - Type and specifications
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- Summary and conclusions
- Acknowledgements

Introduction

- Where might one find H_2 sensors?
  - In the hydrogen generation process from carbon-containing fuel reforming or electrolysis;
  - In hydrogen storage and distribution, at production sites and filling stations; and
  - In hydrogen fuel cell/combustion systems. These can be stationary, for example power production or uninterruptible power supply, or mobile, for example automotive.
- Why do we use H_2 sensors?
  - To detect leaks in the system
  - To monitor hydrogen concentrations in experiments
  - To monitor hydrogen concentrations in fuel cells

Sensor Capability Wish List

- Sensor range
  - 0-10 % v/v for safety
  - 0-100 % v/v for fuel cell systems
- Safe performance
- Reliable and accurate
  - Low uncertainty in the readings
- Stable signal with low noise
- Robustness
- Low sensitivity to
  - Temperature
  - Pressure
  - Relative humidity
  - Gas flow rates
- Fast response and recovery time
- Long life time
- Low cross sensitivity
- Low power consumption
- Low cost
- Small size
- Simple installation and maintenance
  - Long service intervals
- Simple integration into the system

We are not asking a lot of the sensors then …

Types of Hydrogen Sensors—1(2)

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- There are a number of different types of hydrogen sensors
  - The method of detecting the gas differs
  - Their range of applicability
  - Their sensitivity to environmental conditions
    - Temperature
    - Pressure
    - Relative humidity
    - Other gases
  - Their response time
    - Usually expressed in terms of t_{90}
  - Their accuracy / resolution
  - Their susceptibility to poisoning

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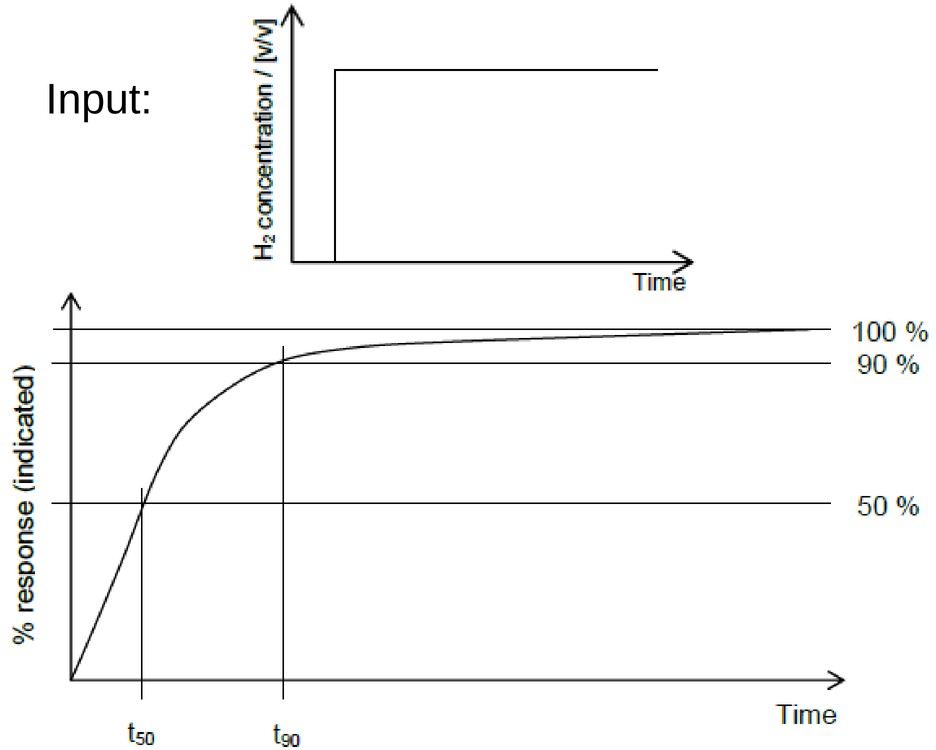

The response time t_{90} is defined as the time it takes for the output from the sensor to reach 90 % of its final value after being subjected to a step change in concentration

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Types of Sensors—(2/2)

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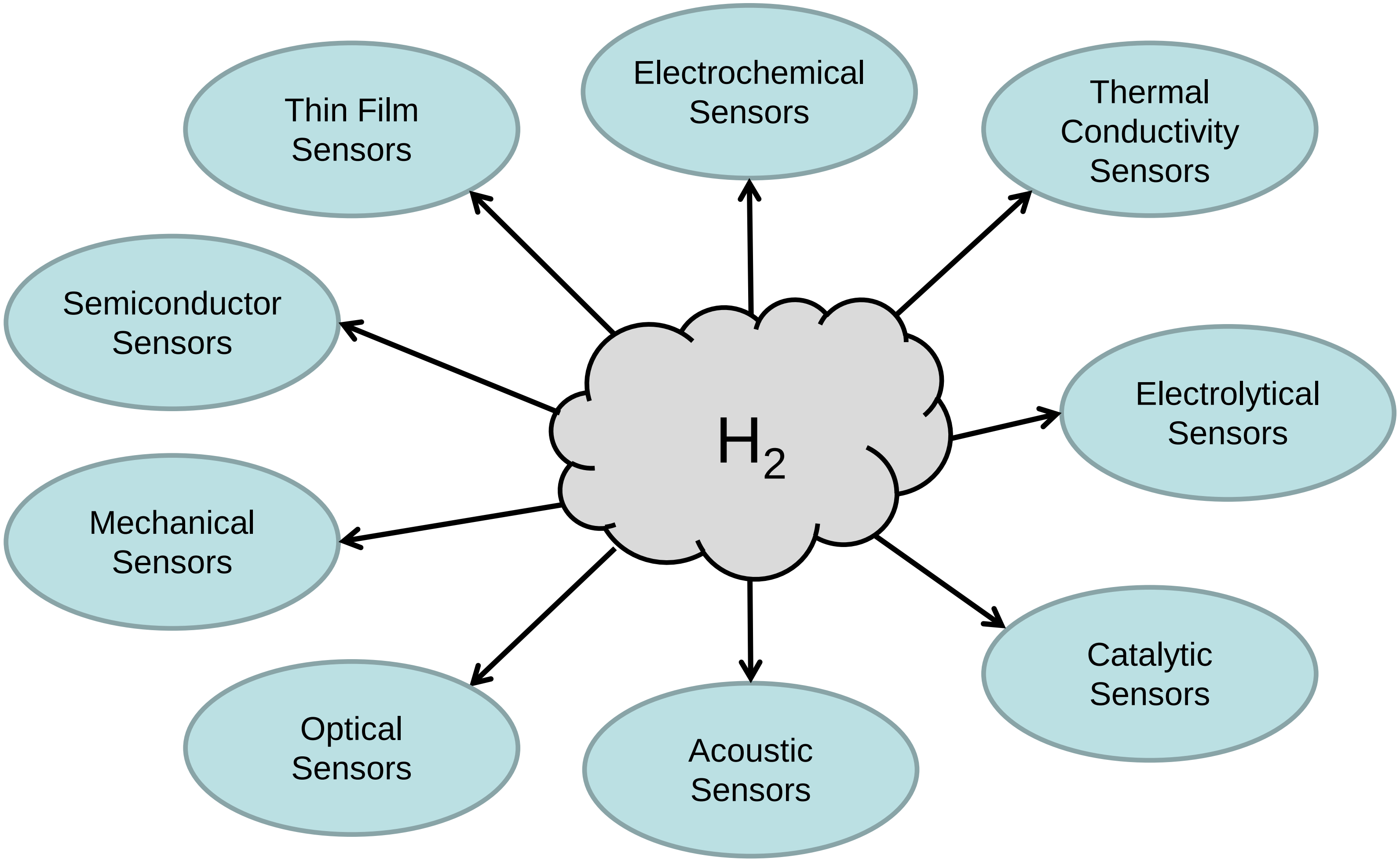

Types of Sensors—1(4)

Type	***Principle***	***Advantages***	***Disadvantages***
Electrochemical	H_2 oxidation at Platinum sensing electrode	• Quite selective • Low power consumption • Poison resistant	• Some cross-sensitivity to CO • Narrow temperature range • Short lifespan of 2 years
Thin film	Reversible resistance increase	• Rapid response • Wide detection range • Does not need O_2	• Prone to poisoning • Sensitive to total pressure • Requires heating to 150 °C

Types of Sensors—2(4)

Type	*Principle*	*Advantages*	*Disadvantages*
ChemFET	Hydrogen absorption	• Wide detection range • Does not need O_2 • Low power consumption	• Prone to poisoning • Sensitive to total pressure • Needs to be heated to 150 °C
Catalytic	Catalytic oxidation on heated bead	• Acceptable lifespan(?) • Wide operational temperature range	• Not selective • High power consumption • Poisoning • Requires 5-10 % v/v O_2 • High maintenance

Types of Sensors—3(4)

Type	*Principle*	*Advantages*	*Disadvantages*
Thermal conductivity	High thermal conductivity changes	• Quite selective • Poison resistant • Long term stability • Does not require O_2	• Not as sensitive as ChemFETs • Cross-sensitive to helium • Requires heating
Semiconductor	Surface conductivity changes	• Commercially available • Acceptable lifespan	• Not selective • High power consumption • Sensitive to humidity and temperature

Types of Sensors—4(4)

Type	***Principle***	***Advantages***	***Disadvantages***
Mass Spectrometry	Charge change detector	• Specific • Low limit of detection	• Expensive • Bulky • Fragile • Needs skilled operator
Ultrasonic	Detection of ultra sound	• Not susceptible to poisoning or humidity • Non-directional	• Not specific to H_2 • Interference from background noise • Only detects high pressure leaks

Comparison of Sensor Types

Type	***Range[1]***	***Resolution[1]***	***Response [s]***	***Lifespan [years]***
Electrochemical	0.0-0.2 % 0.0-2.0 %	2-10 ppm	30	1-2
Thin film + ChemFET	0.1-100 % 10-1000 ppm (with ChemFET)	0.1 % 10 ppm (with ChemFET)	5	?
Catalytic	0-100 % LEL	1 % LEL	20	3
Thermal conductivity	0.0-10 %	0.5 % range	20	10+
Semiconductor	50-5000 ppm	50 ppm	30	?

Note: the lifespan of a sensor depends on a number of factors, for example where it is mounted, the environmental conditions in which it operates, maintenance regime, …

1. Beware of change of units

Sensor Development—1(3)

Type	***Principle***	***Advantages***	***Disadvantages***
Thick film	Resistance change	• Low cost • Simple method	• Susceptible to poisoning
Optoelectronic	• Induced mechanical stress • Interferometry • Optical characteristics	• Very low power consumption • No electromag-netic inter-ference • Intrinsically safe	• Sensitive to humidity and temperature
Nanotechnology	Electrical resistance	• Unproven	• Unproven

Sensor Development—2(3)

Type	*Principle*	*Advantages*	*Disadvantages*
MOS Schottky diodes	Change in electronic properties	• Low concentrations detected • Can operate in inert and oxygen-containing atmospheres	• Response affected by presence of O_2
Surface acoustic wave	Sorption $\Rightarrow$ change of resonance frequency	• Low power • Micro-scale	• Susceptible to water vapour

This is by no means an exhaustive list

Sensor Development—3(3)

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- Introduction of mobile fuel cell applications (for example cars) in particular is driving the sensor technique development forward
- Techniques under development (in reduced order of research activity)
  - Electrical resistance based technologies (40 %)
  - Optical sensors (15 %)
  - Catalytic sensors (5 %)
  - Electrochemical sensors (5 %)
  - Acoustic sensors

Reference:
Hübert, T., Boon-Brett, L., Black, L., and Banach, U. (2011). Hydrogen Sensors-A review, *Sensors and Actuators B* **157**(2):329-352.

Issues with Sensors

- There are a number of operational issues
  - Accuracy and range
  - Calibration—frequent and/or tricky
  - Drifting
  - Cross-sensitivity to other gases
  - Poisoning by other gases
  - Interference by background noise
  - Longevity
  - Response time
  - Sensitivity to pressure, temperature and/or relative humidity
  - False alarms (hydrogen leak detection) / interaction with the system
  - Optimal/appropriate siting
- The sensor type to use is likely
  - To be a compromise; or
  - To be a combination of different types of sensors

Case Study – Hydrogen deflagration in a machine

- In the machine, mechanical parts had metal vapour deposited onto its surface prior to being re-machined
- Hydrogen was being used in the process
- There was a build-up of hydrogen which was detected by the sensor
- However, the system did not shut down
- The hydrogen was ignited, resulting in a deflagration that injured the operator and caused damage to the machine

Lesson: Use hydrogen sensors to detect build-up of hydrogen, but also ensure that an “alarm” is acted upon.

When Things Go Wrong—2(2)

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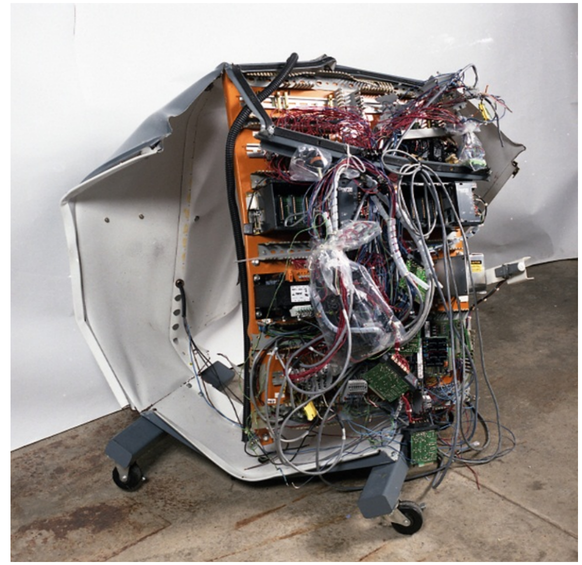
Gas flow meter cabinet—front view

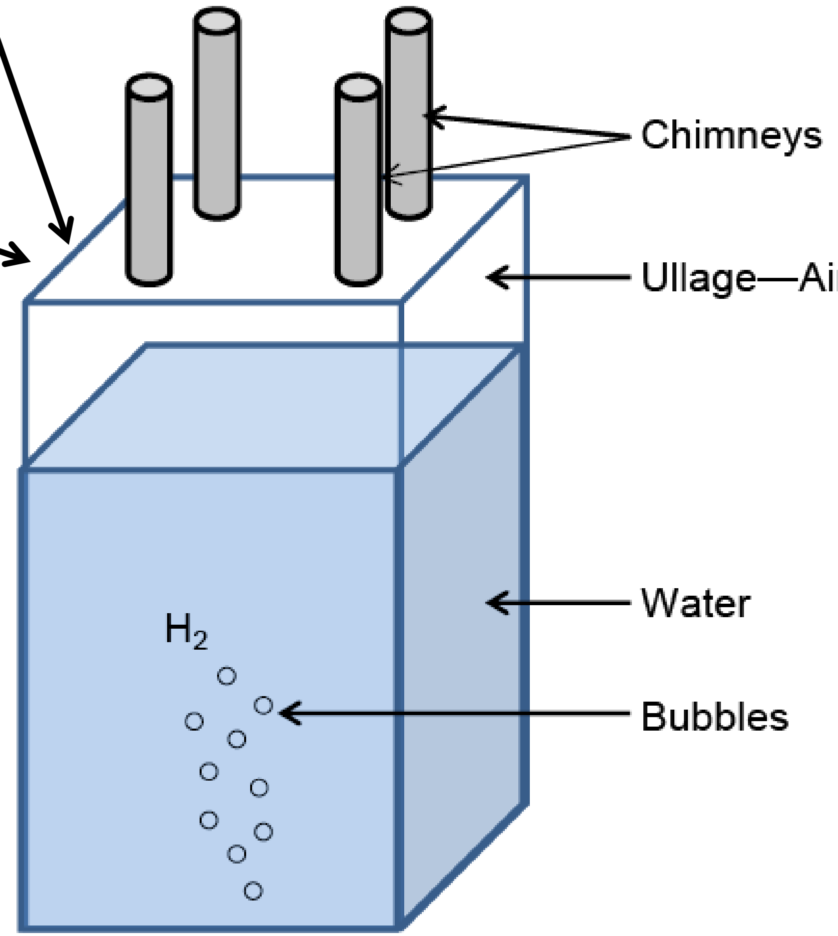


Machine – rear view

Flow meter cabinet – rear view

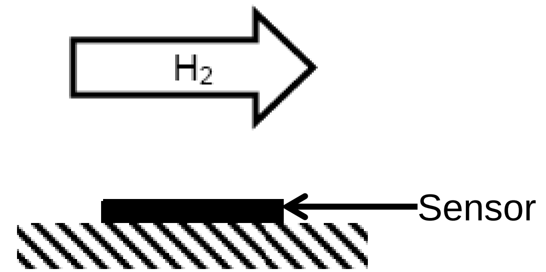
Types of Hydrogen Sensors @ HSL

- XENSOR TCG-3880
  - Thermal conductivity sensor
- SEC H_2 20000 4SE 5V
  - Electrochemical sensor
- VIAMED R17
  - Oxygen depletion sensor

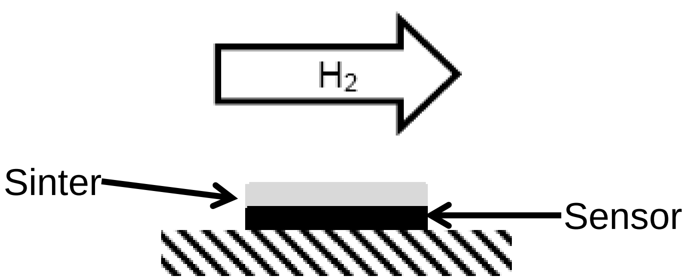


XENSOR TCG-3880

- Thermal conductivity sensor
- Low voltage required: 8-45 mV
- Range: 0-100 % H_2
  - Realistic lower detection limit around 700-1000 ppm
- Readings may be affected by temperature and relative humidity
- Damp conditions can lead to corrosion of leads
- H_2 specific
- Response time:
  - 10 ms —naked sensor
  - 1000 ms — shielded sensor



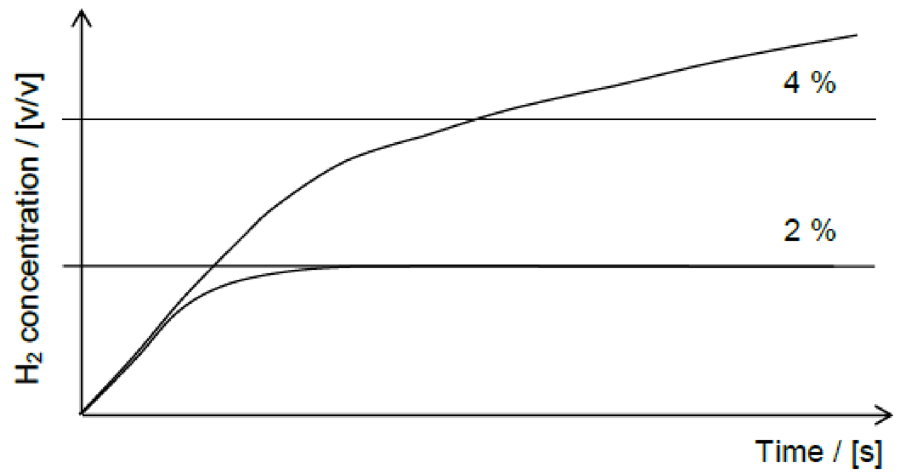
Naked sensor—reading affected by the flow of gas



Shielded sensor

SEC H_2 20000 4SE 5V

- Electrochemical sensor
- Hydrogen specific
- Solid State electrolyte
- Cross-sensitive
- Response time: 10-20 s
- Limited lifespan
  - 1-2 years (though the manufacturer claims 5 years)
  - Electrolyte is consumed
- Range:
  - 0-2 % v/v H_2 (std)
  - 0-4 % v/v H_2 (max)



- Sensor reading keeps drifting when using the 0-4 % v/v range ⇒
  - Calibration is tricky
  - What is the actual hydrogen concentration?

VIAMED R17

- Oxygen depletion sensor
- Insulated body, exposed head
- Silver foil to reduce effect of solar radiation
- Rapid response: t_{90} of the order of 2 s
- Range: 5-100 % v/v H_2
- Sensitive to
  - Temperature, pressure and relative humidity
    - Poor performance at low ambient temperatures (< 5 °C) due to the compensation algorithm
- Requires frequent calibration
  - 10-20 min runtime max

Sensor in-situ

Why We Choose These Sensors

- VIAMED – Oxygen depletion sensor
  - Partly for historical reasons
  - This was almost the only available type of sensor at the time
- XENSOR TCG-5830 – Thermal conductivity sensor
  - Low voltage requirement
  - Fast response time
- SEC H_2 2000 4SE 5V – Electrochemical sensor
  - Hydrogen specific
- Experience from the Instrumentation Special Interest Group in the HySafe Network of Excellence (EU FP6)
- XENSOR and SEC sensors are used together and appear to complement each other well

Note: A sensor of oxygen depletion type is not necessarily the most suitable choice of sensor for hydrogen measurements

Summary and Conclusions

Summary

- There are a number of different types of sensors
- Sensor choice-application specific
- Each type has its merits
- HSL has gained extensive experience of using:
  - Thermal conductivity sensors
  - Electrochemical sensors
  - Oxygen depletion sensors
- What we experienced when using the sensors (sensor type dependent!)
  - Rapid response times
  - Drifting
  - Constant recalibrations needed
  - Sensitivity to temperature, pressure and humidity

Conclusions

- These sensors are mostly fit for purpose, but
  - Calibration is vitally important
  - Drifting is an issue
  - Sensitivity to temperature, pressure and humidity
  - Poisoning or cross-sensitivity
- Oxygen depletion sensors are perhaps not the best option for hydrogen concentration measurements
- A combination of thermal conductivity and electrochemical sensors appears to work well
- A number of “new” technologies are coming on-stream

Acknowledgements

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Thank You for Your Attention!

Any Questions?