Introduction to impurity risk assessment

Thor Anders Aarhaug, SINTEF

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What is Risk Assessment?

- A systematic process of evaluating the potential risk that may be involved in a projected activity
- A combined effort of
    - Identifying and analyzing potentially undesirable events (risk analysis)
    - Judging tolerability while considering influencing factors (risk evaluation)
- A risk assessment determines possible mishaps, their likelihood and consequences, and the tolerances for such events
- RA part of broader Risk Management strategy where control measures are introduced to reduce or eliminate risks
- Qualitative and quantitative assessments

HSE: RA

- How to assess the risks in your workplace?

1. Identify hazards
2. Decide how might be harmed
3. Evaluate risks and decide on precautions
4. Record your significant findings
5. Review your assessment and update if necessary

Qualitative Risk Assessment

- Risk is the product of
  - Probability of occurrence
  - Impact of event
- Verbal evaluation (e.g. very unlikely, major injury)

$$R = P * I$$

LIKELIHOOD			
Very likely	Acceptable risk Medium	Unacceptable risk High	Unacceptable risk Very high
Likely	Acceptable risk Low	Acceptable risk Medium	Unacceptable risk High
Unlikely	Acceptable risk Low	Acceptable risk Low	Acceptable risk Medium
	Low	Medium	High
	IMPACT		

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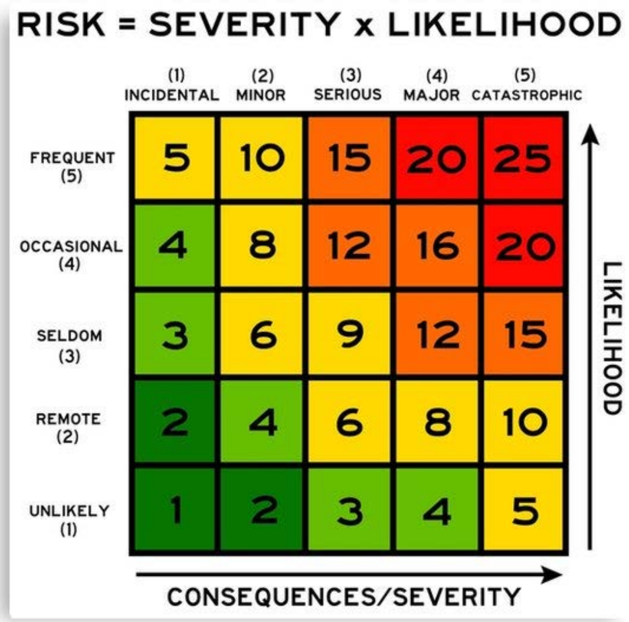
Semi-quantitative risk assessment

- Translate verbal scale into numbers
- Avoid ambiguities (resolution)
- From ISO 19880-8:

Occurrence class	Class name	Frequency
0	Very unlikely	0 (Never)
1	Very rare	1 in 1 M fuellings
2	Rare	1 in 100K fuellings
3	Possible	1 in 10K fuellings
4	Frequent	Often



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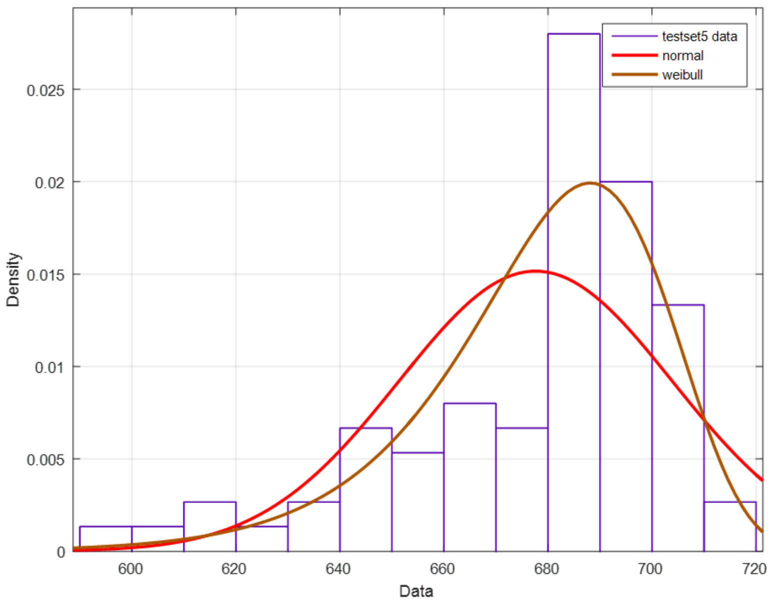
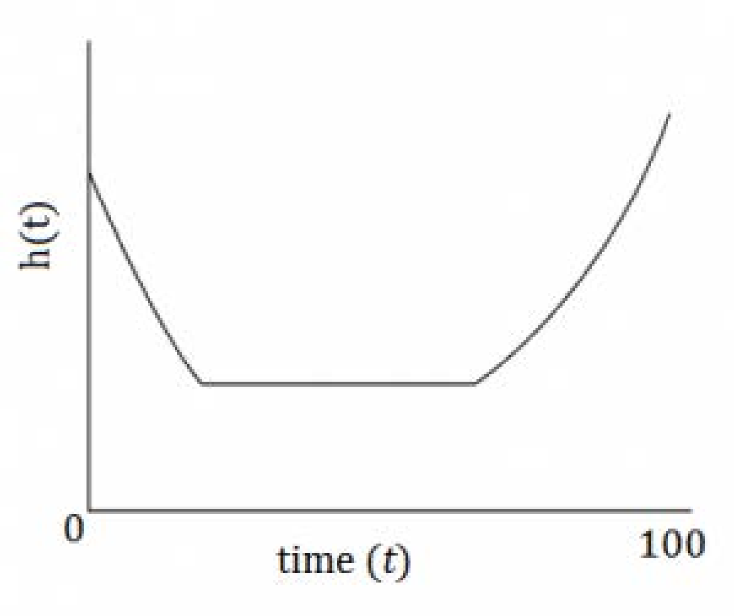
Quantitative risk assessment

- Mathematical modelling of probability and impact
- Population statistics



PEM Stack voltage distibution



Hazard function

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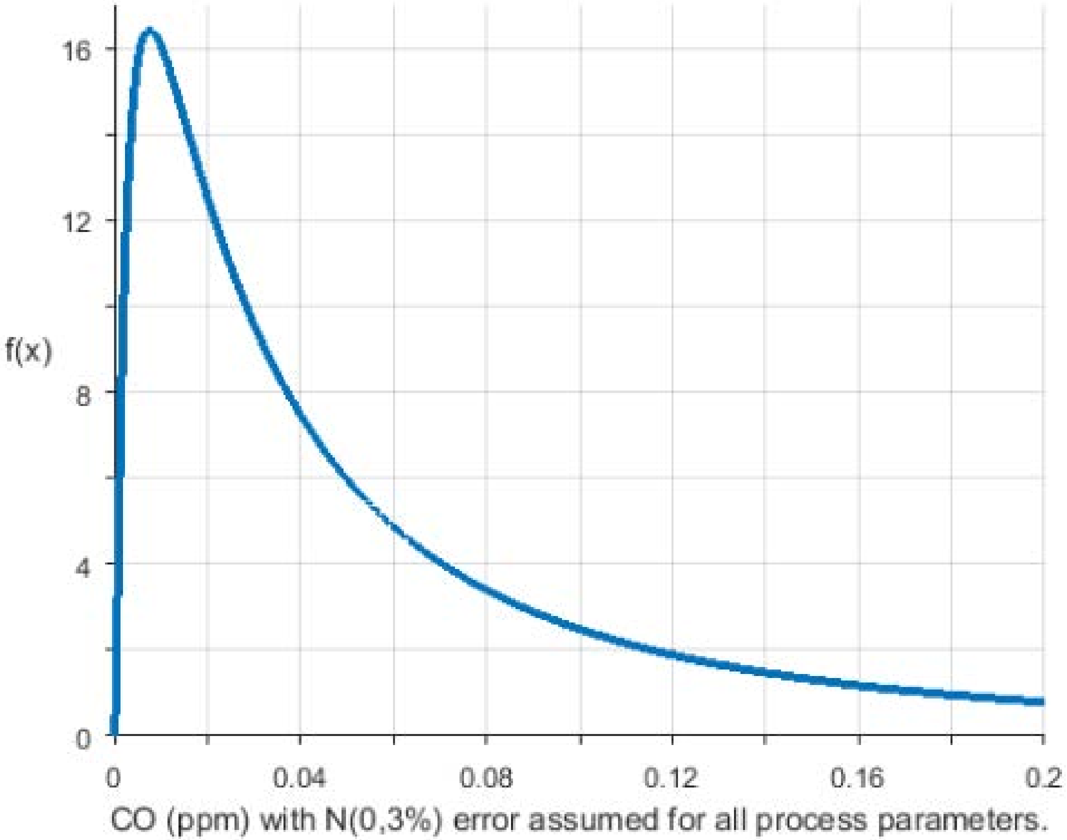
Quantitative RA: HyCoRA

- CO concentration in hydrogen produced from NG-SMR-PSA
- ANL simulation model
- Lognormal probability distribution
- RA model further developed in HYDRAITE



Quality Risk Assessment

- **Objective:**

  For each H_2 source : Evaluation of the risk if there are impurities above their threshold value

- **Risk assessment methodology according to ISO:IEC Guide 73**
- **3 fundamental questions:**

  What might go wrong: which event can cause the impurities to be above the threshold value?

  What is the likelihood (probability of occurrence) that impurities can be above the threshold value?

  What are the consequences (severity) for the fuel cell car?

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RA examples: P of impurities in Steam Methane Reforming

Table 4 – Probability of occurrence of impurities (P) in SMR process with the different barrier existing in the process.

Contaminant	Thresold [µmol/mol]	Cause possible for the source studied	Existing barrier	P
Inert gas: N_2	100	Raw material PSA malfunction	PSA	3
Inert gas: Ar		Raw material		2
Oxygen	5	Not expected to be present.		0
Carbon dioxide	2	Raw material	PSA	0
Carbon monoxide	0.2	Raw material	PSA CO sensor on line	4
Methane (CH_4)	100	Raw material	PSA methane sensor on line	2
Water	5	Raw material	PSA	2
Total sulphur components	0.004	Raw material	Desulfuration unit Sulphur trap in reforming system (poisoning/process operation) PSA Stainless steel pipe and vessl	0
Ammonia	0.1	Raw material	PSA	0
Total hydrocarbons	2	Trace of hydrocarbons after reforming process	PSA	0
Formaldehyde	0.01	Raw material	PSA	1
Formic acid	0.2	Raw material	PSA	0
Helium	100	Not expected to be present.		0
Halogenated compounds	0.05	Raw material	Desulfuration unit Chlorinated trap in reforming system (poisoning/process operation) PSA Stainless steel pipe and vessel	0

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RA examples: P of impurities in Water Electrolysis

Table 5 – Probability of occurrence of impurities (*P*) in Water PEM electrolysis process with the different barrier existing in the process.

Contaminant	Thresold [μmol/mol]	Cause possible for the source studied	Existing barrier	P
Inert gas: N_2	100	Maintenance/start-up phase Leakage Air intake into water tank	Operating procedure (maintenance/restart) PEM membrane cross over H_2 operating procedure > N_2 pressure supply	2
Inert gas: Ar		Not expected to be present.		0
Oxygen	5	Generation at the anodic side of cell stack Membrane cross over TSA malfunction	TSA operating condition Oxygen sensor Operating procedure (maintenance/restart)	2
Carbon dioxide	2	Water at anodic side Air into the pure water tank	CO_2 filter reverse osmosis purification unit for water Anodic separator tank Ion exchange resin in closed water loop PEM membrane	1
Carbon monoxide	0.2	Not expected to be present.		0
Methane (CH_4)	100	Not expected to be present.		0
Water	5	Reactant Through PEM membrane Hydrogen water saturated TSA malfunction	TSA dryer Dew point monitor Operating procedure	2
Total sulphur components	0.004	Not expected to be present.		0
Ammonia	0.1	Water at anodic side	Reverse osmosis purification unit PEM membrane	0
Total hydrocarbons	2	Not expected to be present.		0
Formaldehyde	0.01	Not expected to be present.		0
Formic acid	0.2	Not expected to be present.		0
Helium	100	Not expected to be present.		0
Halogenated compounds (organo-halogenated)	0.05	Water at anodic side	Reverse osmosis purification unit	0
Halogenated compounds (Cl_2)	0.05	From process/higher pressure of hydrogen rather than Cl_2	Safety monitoring at the anode/Separation of Cl_2 and H_2 by the process/detected due to faster diffusivity of hydrogen gas/process would be shut down in time to avoid contamination of hydrogen with Cl_2(g).	0
Halogenated compounds (HCl)	0.05	Conversion of Cl_2(g) would be likely to convert into HCl(g) at the catalyst surfaces.	Chemical reaction (negative Gibbs free energy)/Cl_2 is unlikely to be present	0

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RA examples: P of impurities in Chlor-alkali process

Table 6 – Probability of occurrence of impurities (P) in Chlor-alkali process with the different barrier existing in the process.

Contaminant	Thresold [μmol/mol]	Cause possible for the source studied	Existing barrier	P
Inert gas: N_2	100	Maintenance/start-up phase		2
Inert gas: Ar		Not expected to be present.		0
Oxygen	5	can be present		4
Carbon dioxide	2	Oxidation of organic matter in the brine. Degradation of the membrane on the cathode side made of conducting by carboxylic acid end groups	Chemical reaction (CO_2 is expected to remains in the caustic soda lye that is produced)	1
Carbon monoxide	0.2	Not expected to be present.		0
Methane (CH_4)	100	Not expected to be present.		0
Water	5	can be present/Process parameter	Drying system to a dew point below - 20 °C (dew point: ~40–60 °C)	2
Total sulphur components	0.004	Not expected to be present.		0
Ammonia	0.1	Not expected to be present.	Use of pure water (demineralised water)	0
Total hydrocarbons	2	Not expected to be present.		0
Formaldehyde	0.01	Not expected to be present.		0
Formic acid	0.2	Not expected to be present.	Use of pure water (demineralised water)	0
Helium	100	Not expected to be present.		0
Halogenated compounds (organo-halogenated)	0.05	Not expected to be present.		0
Halogenated compounds (Cl_2)	0.05	From process/higher pressure of hydrogen rather than Cl_2	Safety monitoring at the anode/ Separation of Cl_2 and H_2 by the process/detected due to faster diffusivity of hydrogen gas/process would be shut down in time to avoid contamination of hydrogen with Cl_2(g).	0
Halogenated compounds (HCl)	0.05	Conversion of Cl_2(g) would be likely to convert into HCl(g) at the catalyst surfaces.	Chemical reaction (negative Gibbs free energy)/Cl_2 is unlikely to be present	0

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Impact classification (ISO 19880-8)

<table>
<tr><th>Severity class</th><th>FCV impact</th><th>Performance impact</th><th>Hardware temporary</th><th>Hardware permanent</th></tr>
<tr><td>0</td><td>None</td><td>No</td><td>No</td><td>No</td></tr>
<tr><td>1</td><td>Minor impact
Temporary power loss
Still in operation</td><td>Yes</td><td>No</td><td>No</td></tr>
<tr><td>2</td><td>Reversible damage
Requires specific light maintenance
Still in operation</td><td>Yes or No</td><td>Yes</td><td>No</td></tr>
<tr><td>3</td><td>Reversible damage
Requires specific immediate maintenance
Gradual power loss that does not compromise safety</td><td>Yes</td><td>Yes</td><td>No</td></tr>
<tr><td rowspan="2">4</td><td rowspan="2">Power loss or vehicle stop that compromises safety
Irreversible damage
Requires major repair procedure</td><td rowspan="2">Yes</td><td>Yes</td><td>No</td></tr>
<tr><td>No</td><td>Yes</td></tr>
</table>

Combined RA (ISO 19880-8)

Probability per one fuelling	Occurrence	Severity				
		0	1	2	3	4
Frequent: Often	4	+	*	*	*	*
Possible: 10^{-4}	3	+	o	*	*	*
Rare: 10^{-5}	2	+	+	o	*	*
Very Rare: 10^{-6}	1	+	+	+	o	*
Practically Impossible	0	+	+	+	+	+
Key	+ Acceptable risk area: Existing controls sufficient		o Further investigation is needed: existing barriers or control may not be enough		* Unacceptable risk; additional control or barriers required	

Impact on powertrain (ISO 19880-8)

Impurity		ISO 14687-2 threshold value[a] [µmol/mol]	Severity class (from ISO 14687-2 to Level 1)	Level 1 value [µmol/mol]	Severity class (greater than Level 1 threshold)
Total non-H_2 gases		300	1	UD	UD
Total nitrogen and argon	N_2, Ar	100	1[b]	300[a]	4
Oxygen	O_2	5	UD	UD	4[c]
Carbon dioxide	CO_2	2	1	3	4
Carbon monoxide	CO	0,2	2-3[d]	1	4
Methane	CH_4	100	1	300	4
Water	H_2O	5	4	5	4
Total sulphur compounds	H_2S basis	0,004	4	>0,004	4
Ammonia	NH_3	0,1	4	>0,1	4
Total hydrocarbons	CH_4 basis	2	1-4[b]	>2	4
Formaldehyde	CH_2O	0,01	2-3[b]	1	4
Formic acid	HCOOH	0,2	2-3[b]	1	4
Halogens		0,05	4	>0,05	4
Helium	He	300	1	300	4
Maximum particulate concentration (liquid and solid)[e]		1 mg/kg	4	>1 mg/kg	4

Combined RA SMR supply chain (19880-8)

ISO specification		Supply chain probability							Residual			
Impurity	Threshold µmol/mol	Production SMR	Pipeline distribution	Fuelling station	Compounded probability	Severity	Criticality	Additional risk reduction measures	Severity reduction measures	Prob-abili-ty	Se-veri-ty	Criti-cality
Inert gas N_2	100	3	1	3	3	1	o	Systematic N_2 analysis after shutdown before resuming operation or specific purging procedure	None	1	1	+
Inert gas Ar		2	0	0	2	1	+		None	2	1	+
O_2	5	0	1	2	2	0	+		None	2	0	+
CO_2	2	0	0	0	0	1	+		None	0	1	+
CO	0,2	4	0	0	4	2	*	CO absorber at fuelling station design margin 100 % + operation procedure for replacement when H_2 quantity purified = 50 % of design capacity.	None	1	2	+
CH_4	100	2	0	0	2	1	+		None	2	1	+
H_2O	5	0	0	1	1	4	*	Check H_2O at commissioning and after maintenance involving opening of vessels or piping. Measurement shall be done at appropriate location downstream of the considered vessel or piping	None	0	4	+
TS	0,004	0	0	1	1	4	*	Check TS at commissioning and after maintenance involving parts modification (piping, valves, seals, gaskets). Not required for part replaced by identical component	None	0	4	+
NH_3	0,1	0	0	0	0	4	+		None	0	4	+
THC	2	0	0	2	2	4	+	Oil/grease cleaning at commissioning and after maintenance. Compressor surveillance depending on compressor technology (coalescing filter) THC analysis or commissioning and after maintenance	None	0	4	+

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Combined RA SMR supply chain (19880-8)

ISO specification		Supply chain probability			Compounded probability	Severity	Criticality	Additional risk reduction measures	Residual			
Impurity	Threshold µmol/mol	Production SMR	Pipeline distribution	Fuelling station					Severity reduction measures	Prob-abili-ty	Se-veri-ty	Criti-cality
HCHO	0,01	1	0	0	1	2	+		None	1	2	+
HCOOH	0,2	0	0	0	0	2	+		None	0	2	+
Halogens	0,05	0	0	1	1	4	*	Halogenated analysis at commissioning (species shall be defined) or after maintenance	None	0	4	+
He	300	0	0	0	0	1	+		None	0	1	+

Key	+	o	*
	Acceptable risk area: existing controls sufficient	Further investigation is needed: existing barriers or control may not be enough	Unacceptable risk; additional control or barriers required

HYDRAITE RA

- Extend existing RA
  - Chlor-alkali: non-membrane process (chlorate)
  - Water electrolysis: water feed from desalination
- New hydrogen production methods
  - Biomass/pyrolysis (Linde process)
  - Biological hydrogen production
  - Other?

- RA Quantitative modeling

[Acknowledgements…]

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