Duplex Stainless Steel in Heat Exchangers for Alkaline Electrolyzers

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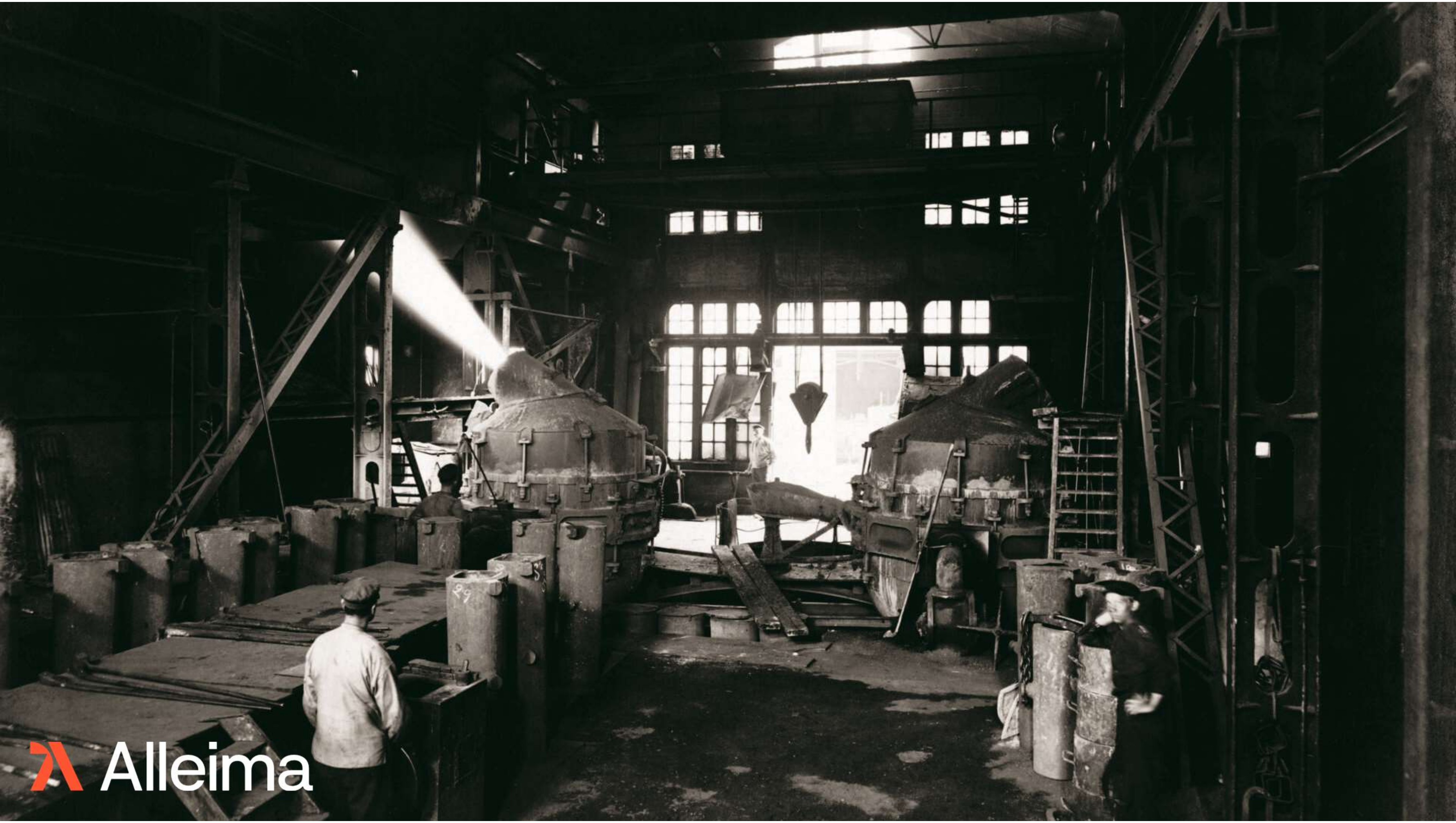
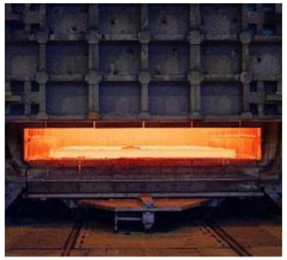

Alleima

Advancing industries through materials technology

Industrial
- Solid round bar and hollow bar
- High pressure tubing
- Composite tubing
- Wear resistance strip

Chemical and petrochemical
- Fertilizer tubing
- Hydraulic and instrumental tubing
- Heat exchanger tubing

Oil and gas
- Umbilical tubing
- Control lines
- Oil Country Tubular



Industrial heating
- Metallic heating elements
- Ceramic heating elements
- Radiant Kanthal® APM / Kanthal APMT® tubes
- Diffusion cassettes

Consumer
- Compressor valve steel
- Stainless knife steel
- Razor blade steel
- Appliance wire

Power generation
- Steam generator tubes
- Cladding tubing
- Nuclear tubes and pipes
- Strip steel spacers

Mining and construction
- Rock drill steel

Transportation
- Titanium and stainless-steel tubes
- Gasoline Direct Injection (GDI) tubes
- Compressor valve steel
- Shock absorber steel

Medical
- Medical precision wire
- Medical tubing
- Medical strip

Hydrogen and renewable energy
- Coated strip steel for fuel cells
- High pressure tubing for hydrogen applications
- High nickel alloy tubing for concentrated solar power applications

Agenda

- **Alkaline electrolyzers**
- **Stainless steels in caustic solutions**
- **Challenges**
- **Conclusions**

Agenda

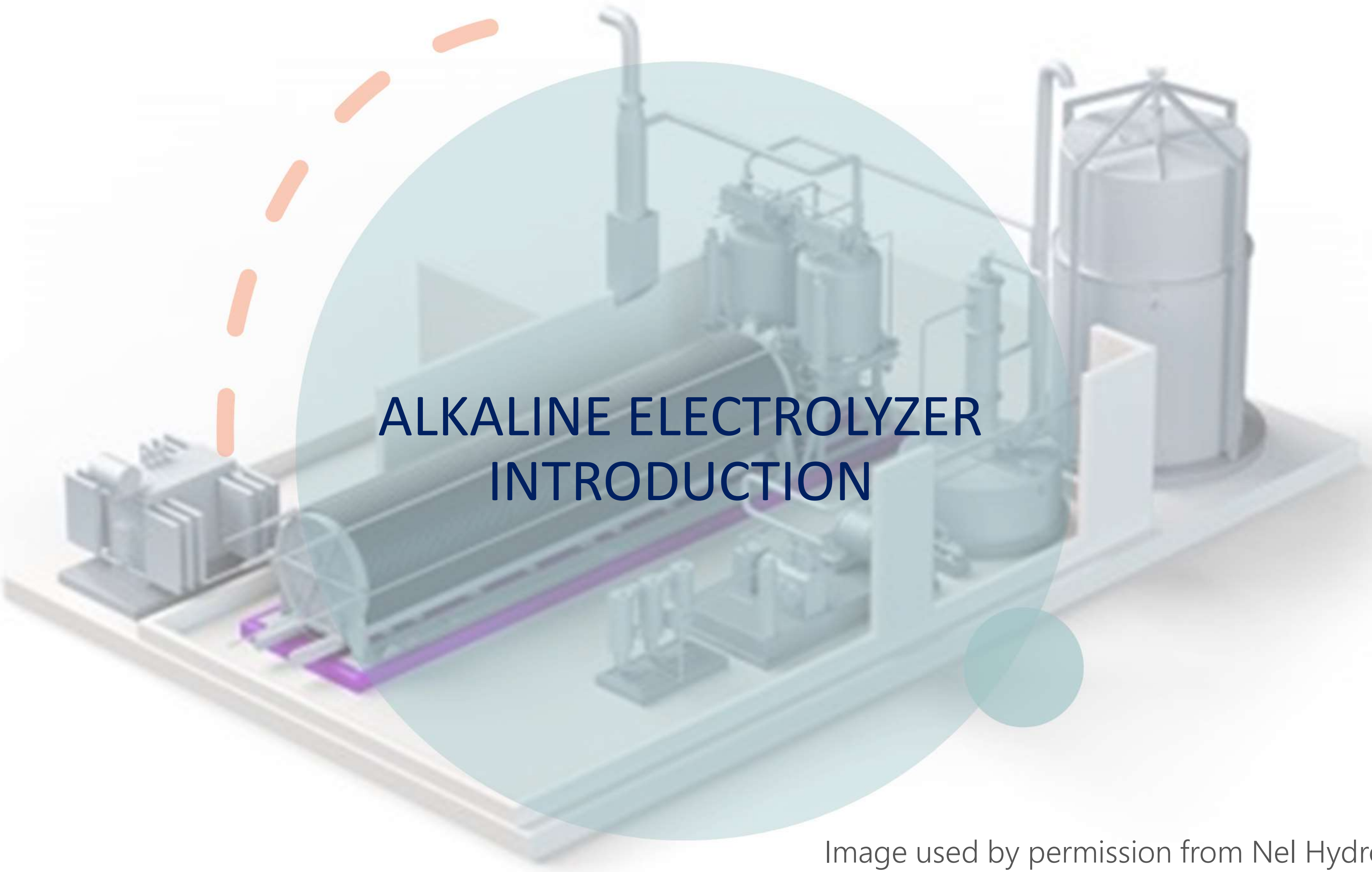
Alkaline electrolyzers

Introduction

Basic operations

Design considerations

ALKALINE ELECTROLYZER INTRODUCTION



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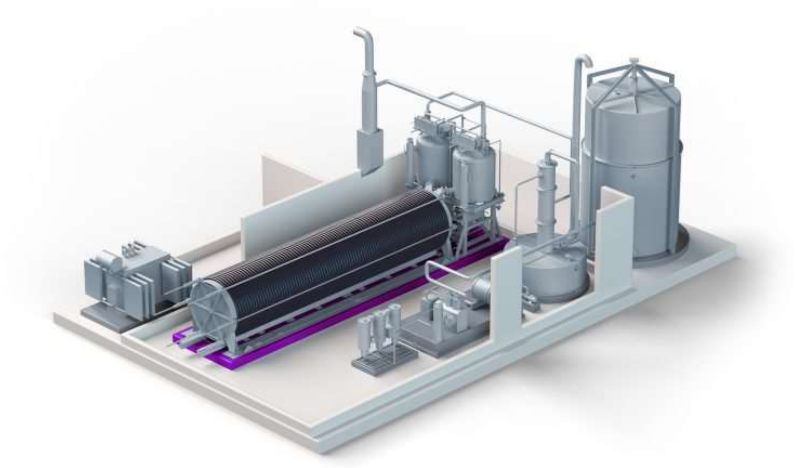
Alkaline electrolyzers – basic operations

- Electrolyte is commonly 25-30% KOH
- Produces hydrogen and oxygen gas by electrolysis of water in an alkaline environment
  - Cathode reaction: $2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2\ OH^-(aq)$
  - Anode reaction: $2\ OH^-(aq) \rightarrow ½O_2(g) + H_2O(l) + 2e^-$
  - **Overall reaction:** $\mathbf{H_2O\ (l) \rightarrow H_2(g) + ½O_2(g)}$

- Operating pressure up to 30 bar
- Operating temperature 80-90°C

Alkaline electrolyzers – design considerations

- Components in the electrolyzer system
  - The cell stack.
  - Piping for electrolyte and electrolyte + gases
  - Gas separators
  - Tanks for electrolyte and water replenishment
  - Heat exchangers for cooling and balance of plant (BOP)
    - Depending on location, freshwater or seawater cooling can be used



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Alkaline electrolyzers – design considerations

– Water is consumed in operation and replenished
  – Any added impurities will build up in the system
    – Water needs to be very clean
  – Corrosion products will build up in the system
    – Can cause problems with catalysts
    – Can cause blockage in small-diameter tubes and pipes.
    – **Materials must be corrosion-resistant to the operating environment**

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Stainless steels in caustic solutions

General information and chemical composition

Corrosion resistance of austenitic and duplex grades

Conversion of corrosion data for NaOH to KOH

General information

- Solutions of sodium or potassium hydroxide ($NaOH$ and KOH) are not corrosive to stainless steel as long as
  - Concentration is not too high
  - Temperature is not too high
- Corrosion mechanisms are
  - General corrosion.
  - Stress corrosion cracking
- 304L austenitic stainless steel has been used successfully for many caustic applications in the pulp and paper industry
  - Reasonable long service life and low replacement cost when using a welded pipe

Stainless steel chemical composition

Typical chemical composition (nominal), %						
Austenitic grades						
Alloy	UNS	C	Cr	Ni	Mo	N
304L	S30403	<0.03	18.5	10	-	
316L	S31603	<0.03	17	11.5	2.1	
904L	S08904	<0.03	20	25	4.5	
Duplex grades						
2304	S32304	<0.03	22.5	4.5	0.3	0.10
2205	S32205	<0.03	22	5	3.2	0.18
2507	S32750	<0.03	25	7	4	0.30
2906	S32906	<0.03	29	7	2.3	0.35

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Corrosion resistance of austenitic and duplex grades

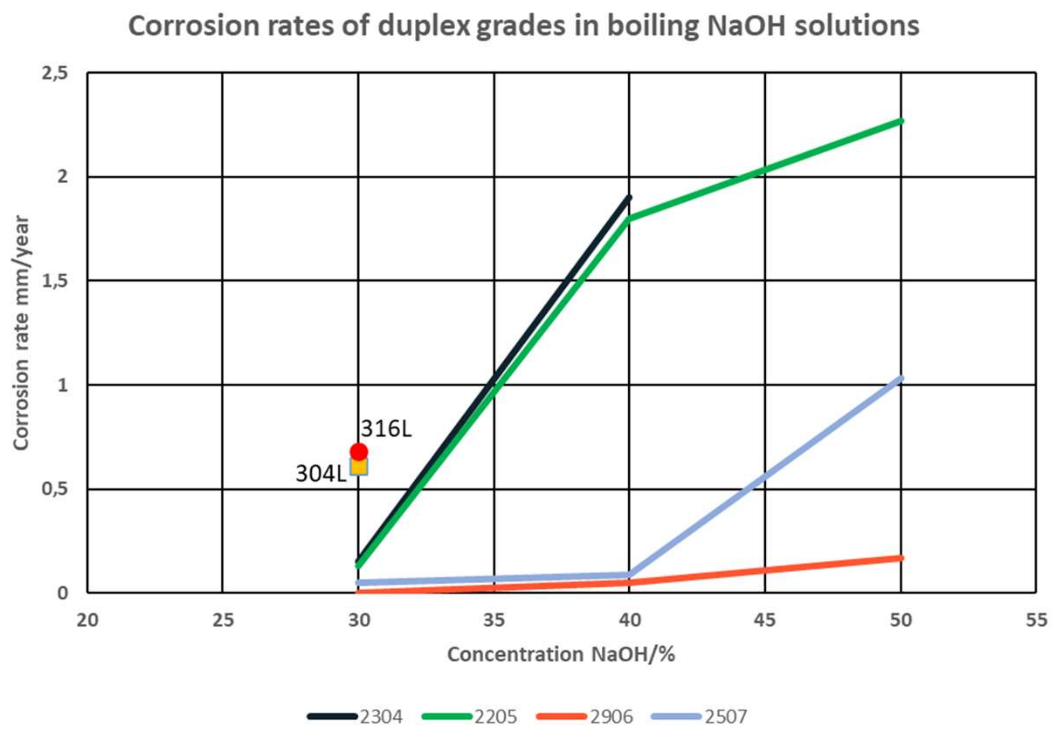
– General corrosion data for selected stainless steel grades in NaOH

Conc. %	10	10	10	20	20	25	25	30	30	30	40	40
Temp. °C	20	90	103=BP	20	90	20	112=BP	20	100	116=BP	80	90
Carbon steel	0			0		0		0				
13 Cr	0	0	1	0	1	0	2	0	1	2	1	1
304L (1.4306)	0	0	0	0	0	0	0	0	0	1s	0	0
316L (1.4435)	0	0	0	0	0	0	0	0	0	0s	0	0
904L	0	0	0	0	0	0	0	0	0	0s	0	0
Duplex 2304	0			0				0	0	0ND	0	0
Duplex 2205	0			0				0	0	0ND		
Duplex 2507	0			0				0	0	0ND		

0 = <0.1mm/y
1 = 0.1 – 1 mm/y
S = Stress corrosion cracking
ND = Not tested
BP = Atmospheric Boiling point
Source: Corrosion handbook stainless steels

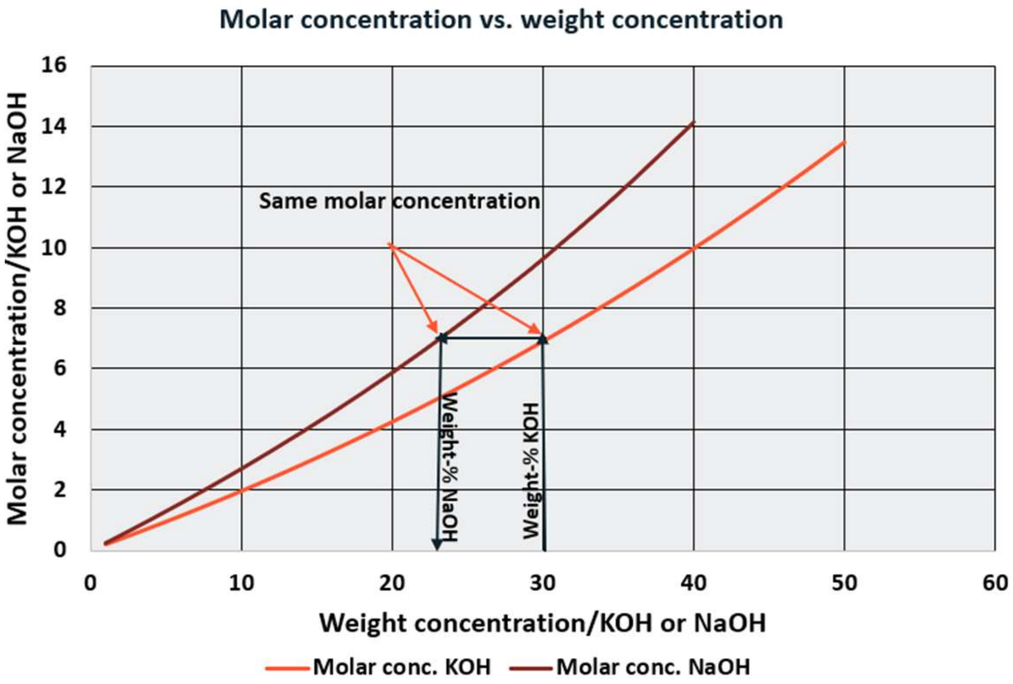
Duplex grades in strong caustic solutions

- In-house testing of duplex grades suitable for caustic service
- Duplex 2304 and 2205 show very similar performance
- Duplex 2906 outperforms the other grades.
  - 0.05 mm/y in boiling 40% NaOH
- Results confirm that higher chromium concentration gives better corrosion resistance.



Conversion of corrosion data for NaOH to KOH

- There is very little published data for corrosion in KOH.
  - Data for NaOH can be used instead.
  - Na+ and K+ do not play an active part in the corrosion process.
- The corrosive part of a caustic solution is the OH- ion.
  - The molar concentration of OH- governs the corrosivity of the solution.
- Potassium is heavier than sodium.
  - 20 weight-% KOH has a lower OH concentration than 20 weight-% NaOH.
  - 20 weight-% NaOH more corrosive than 20 weight-% KOH.
  - 30 weight-% KOH ≈ 23 weight-% NaOH.



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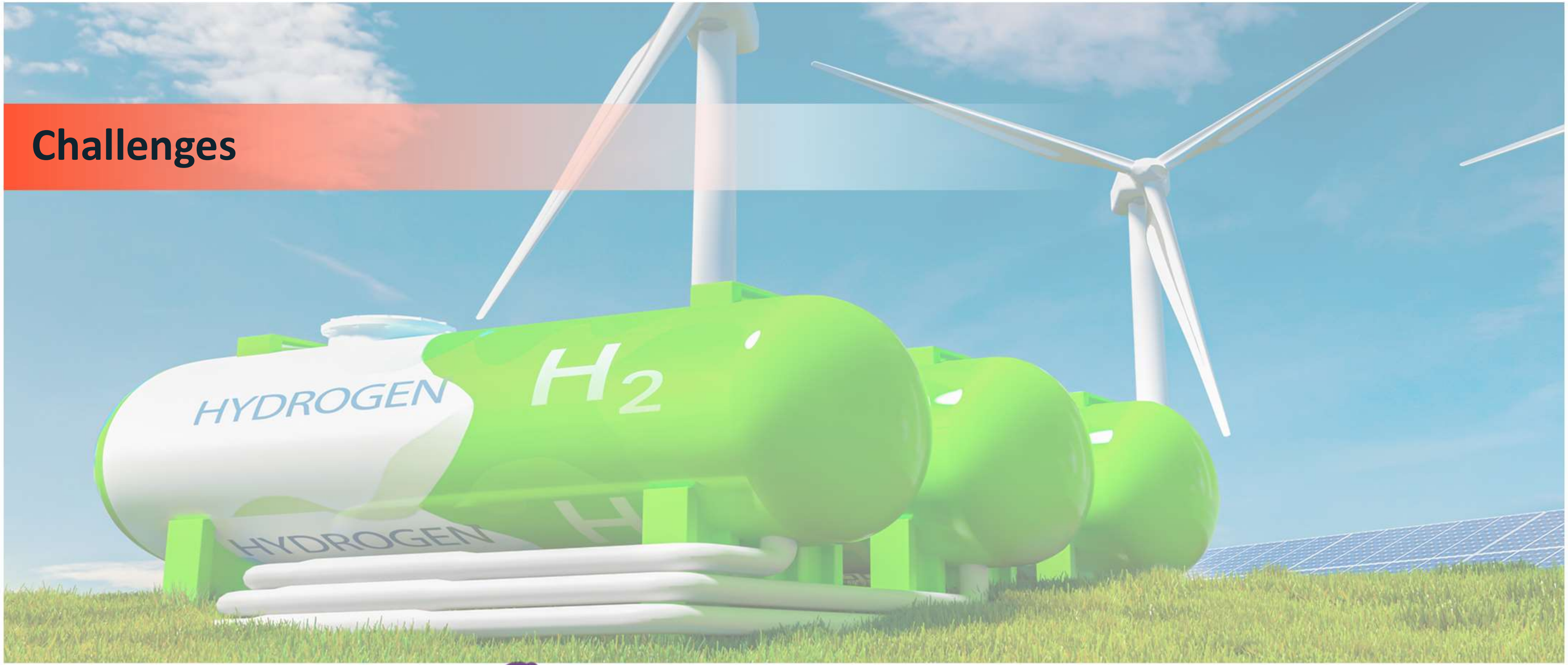
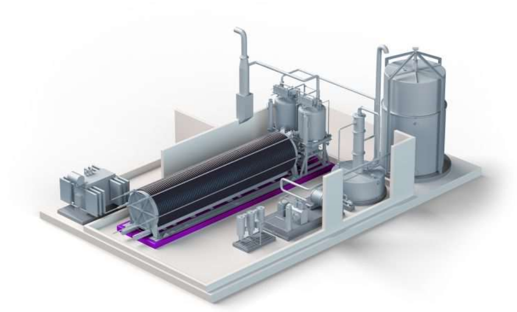


Design criteria



- For some alkaline electrolyzer plants, the design criteria are very tough.
  - 40% KOH (≈ 32% NaOH).
    - Up-concentration when water is consumed.
  - T = 120°C.
  - P = 40 bar.

- Design life >30 years without any replacement of components…
  - Corrosion rates >0.05 mm/y adds up to >1.5 mm/y.
  - No corrosion products allowed.
    - Can cause fouling of piping system, tanks, and cell stack.

Parts after electrolyzer stack and for gas separation are exposed to high pressures of

Hydrogen

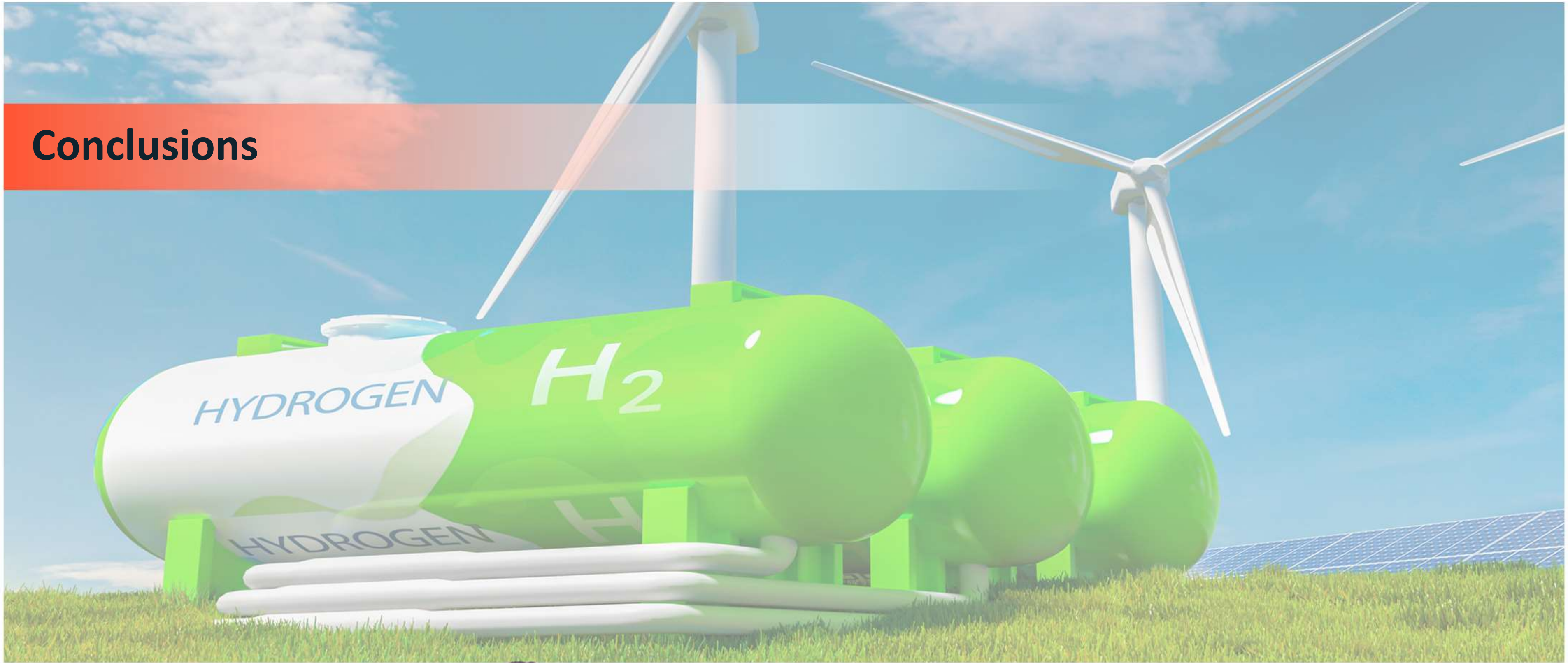
– Cause loos the ductility and embrittlement of
  – Austenitic stainless steels with low nickel content
  – Duplex stainless steels because of the ferrite content
– **Higher alloyed austenitic grades should be considered**

Oxygen

– Increase the risk for SCC of stainless steel grades
– More tests and investigations are necessary to find the best suitable stainless steel grades

Agenda

Conclusions



Conclusions

- Alkaline electrolyzers are well-established in the hydrogen market
  - 300-series stainless steel has served well
- New developments and demands on performance and plant service life make duplex grades highly attractive
- Resistance towards stress corrosion cracking at high oxygen pressures must be investigated
- Suitability of duplex grades in high-pressure hydrogen service is questionable

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