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Low Temperature Reactivity of Aluminum Nanopowders with Liquid Water

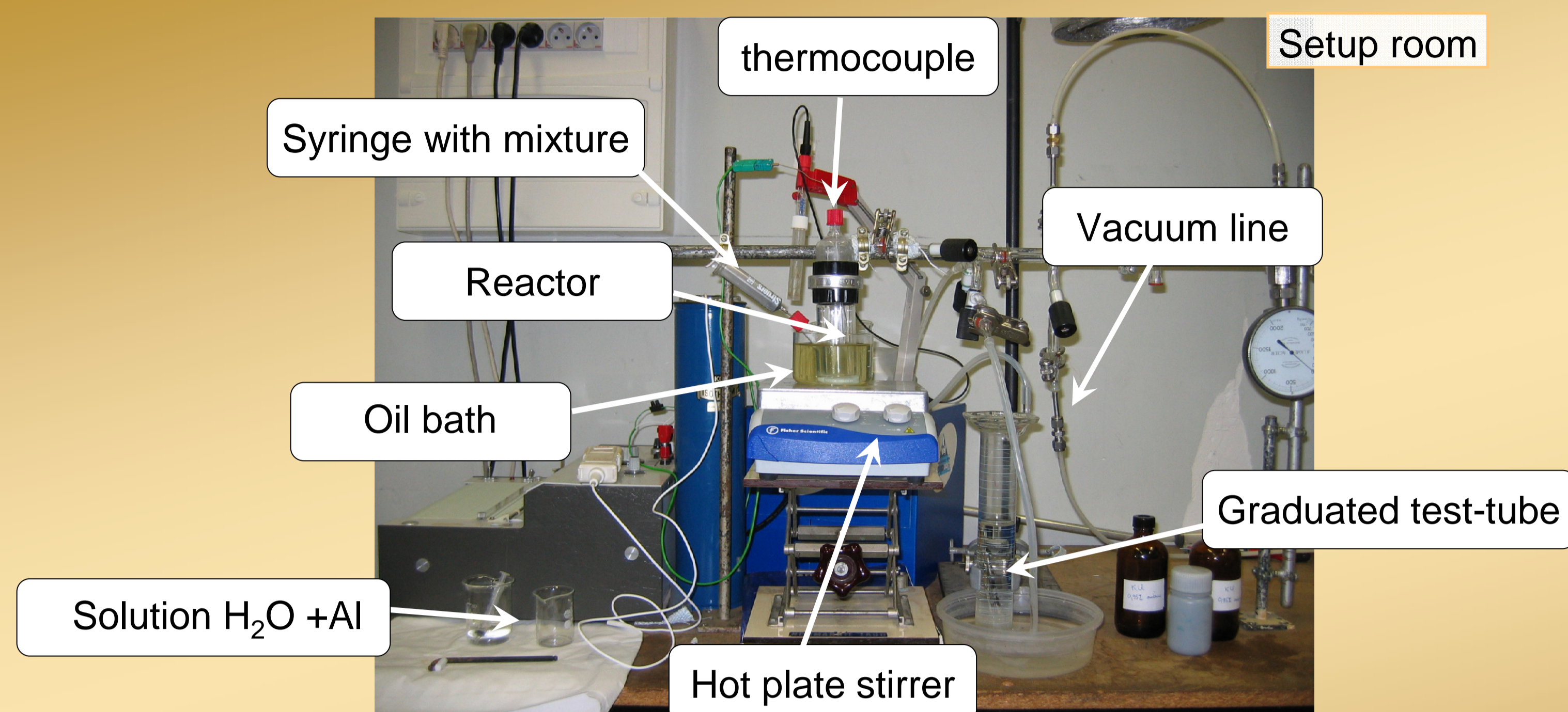
1 - Introduction

- Aluminum nanoparticles react with water and produces hydrogen.
- As hydrogen is envisaged as an alternative energy vector, is it possible to consider Ultrafine Aluminum Powder (UFP) as a in situ hydrogen source ?

2 - Objectives of the present work

- Understanding of the macrokinetics of the hydroxidation of aluminum.
- Measurements of the H₂ gas release rate as a function of time and temperature.
- Investigating the effect of salt water compared to pure water.

3 - Experimental setup



Operating Conditions

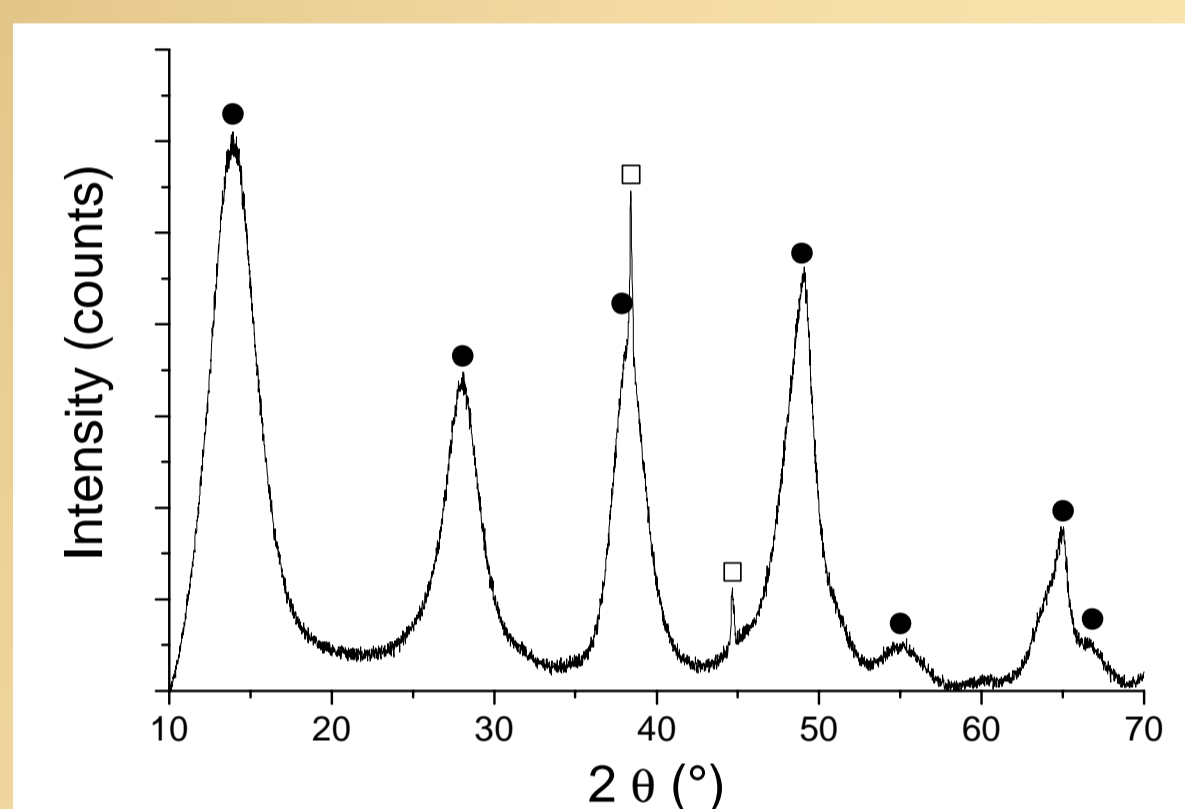
- Isothermal conditions during experiment
- Temperature parameter range [45 – 90 °C]
- Alex powder, air passivated (100 nm mean diameter)
- Mixture composition fixed as:
 - 60 g distilled water
 - 0.1 g of Alex powder
- Saline solution 3% w. (KCl or NaCl)

Experimental Techniques

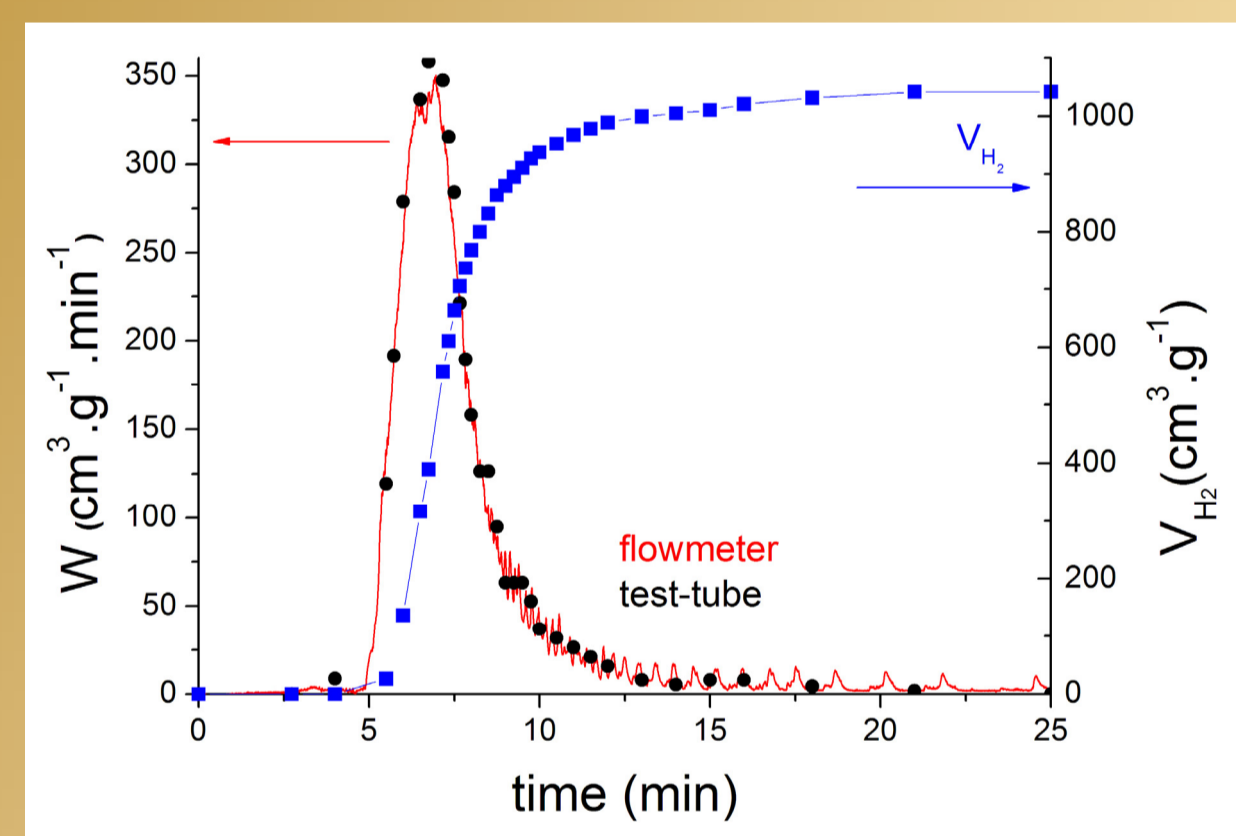
- Temperature ⇒ Thermocouple
- H₂ gas release ⇒ { graduated test-tube
Mass flowmeter
- Transmission electron microscopy
- X-ray diffraction

4 - Results

- X-ray analyses of the solid reaction residues reveal aluminum oxyhydroxide AlOOH (boehmite)
- Gas-phase chromatography confirms the production of gas dihydrogen (H₂)
- $\text{Al(s)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{AlO(OH)(s)} + 3/2 \text{H}_2\text{(g)}$

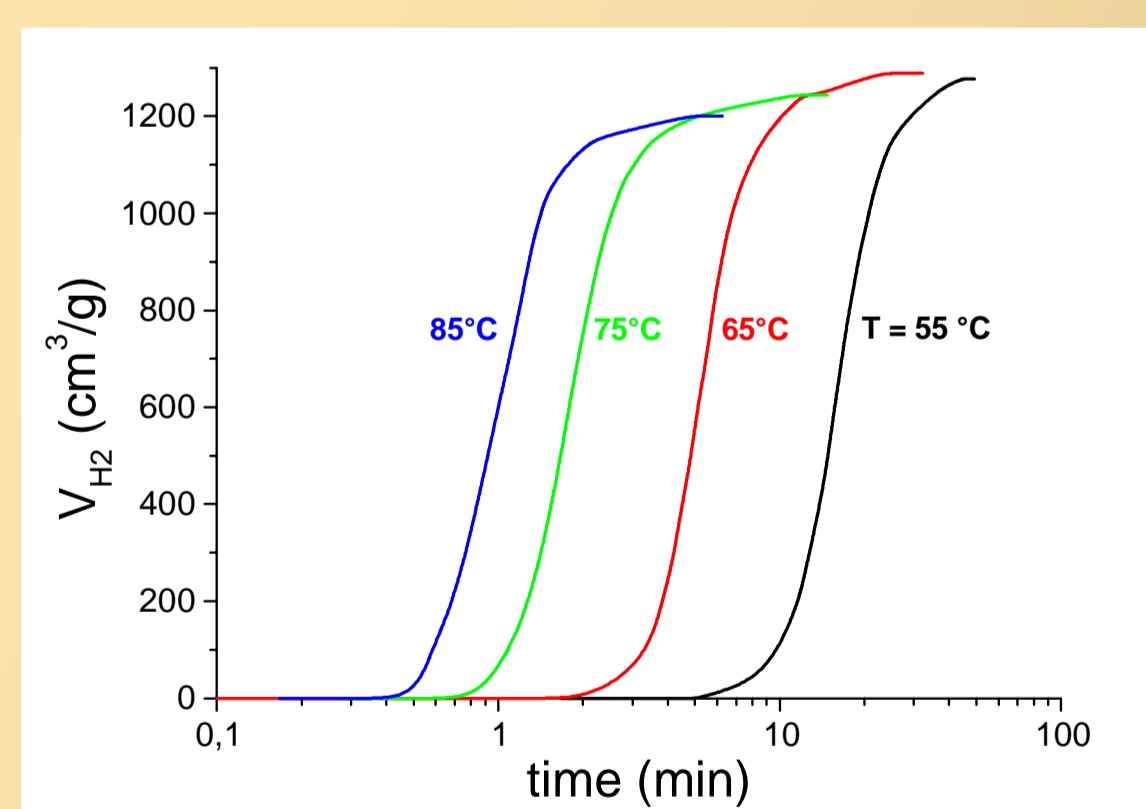


Diffraction diagram of the Al+H₂O reaction residues.
●: AlOOH (JCPDS 00-049-0133);
□: Al (JCPDS 01-085-1327)



Example of an experimental result at T=72°C

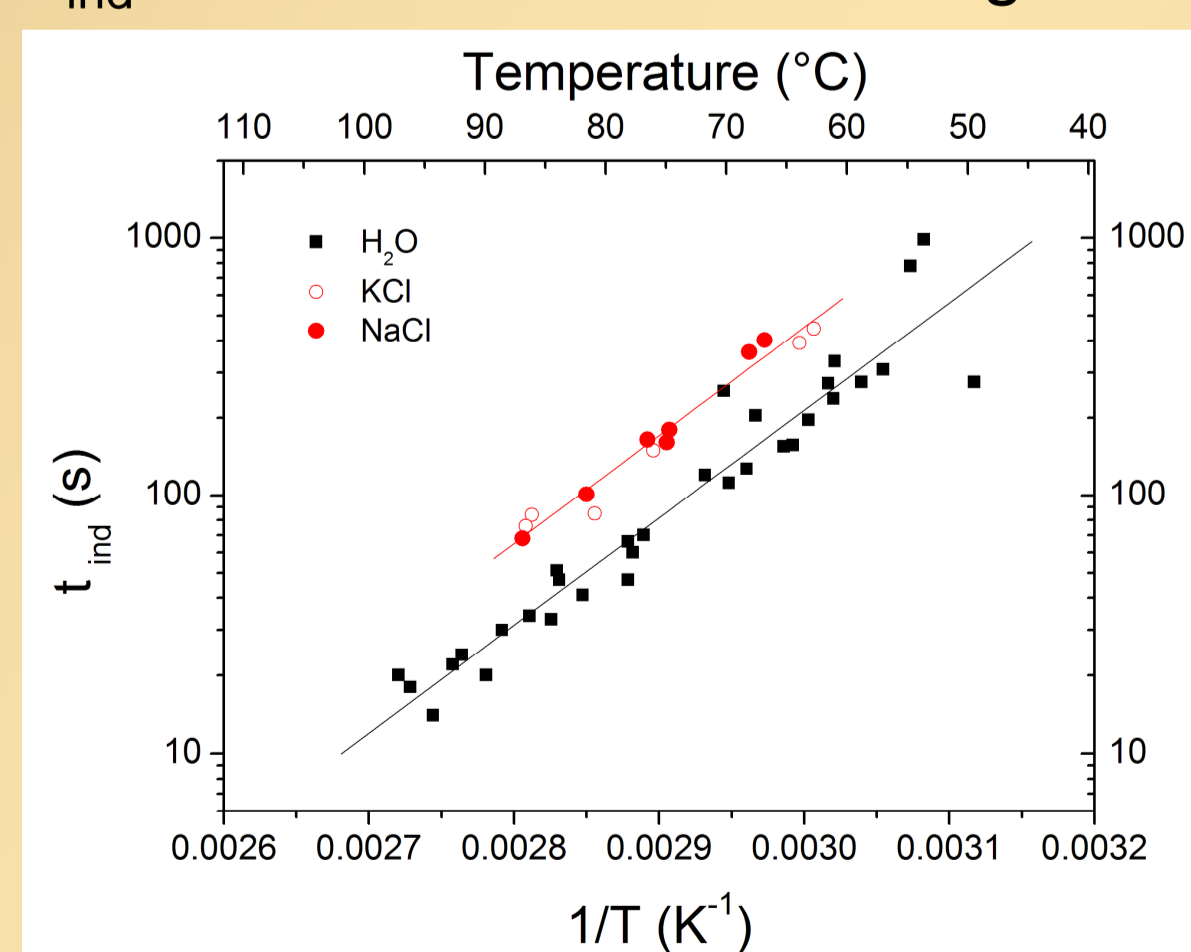
- Reaction starts after an induction period (t_{ind})
- After this period, instantaneous H₂ flow rate increases rapidly, exhibits a maximum then decreases.
- S-shaped gas evolution for the total volume of hydrogen observed.



Gas evolution process in water for different temperatures

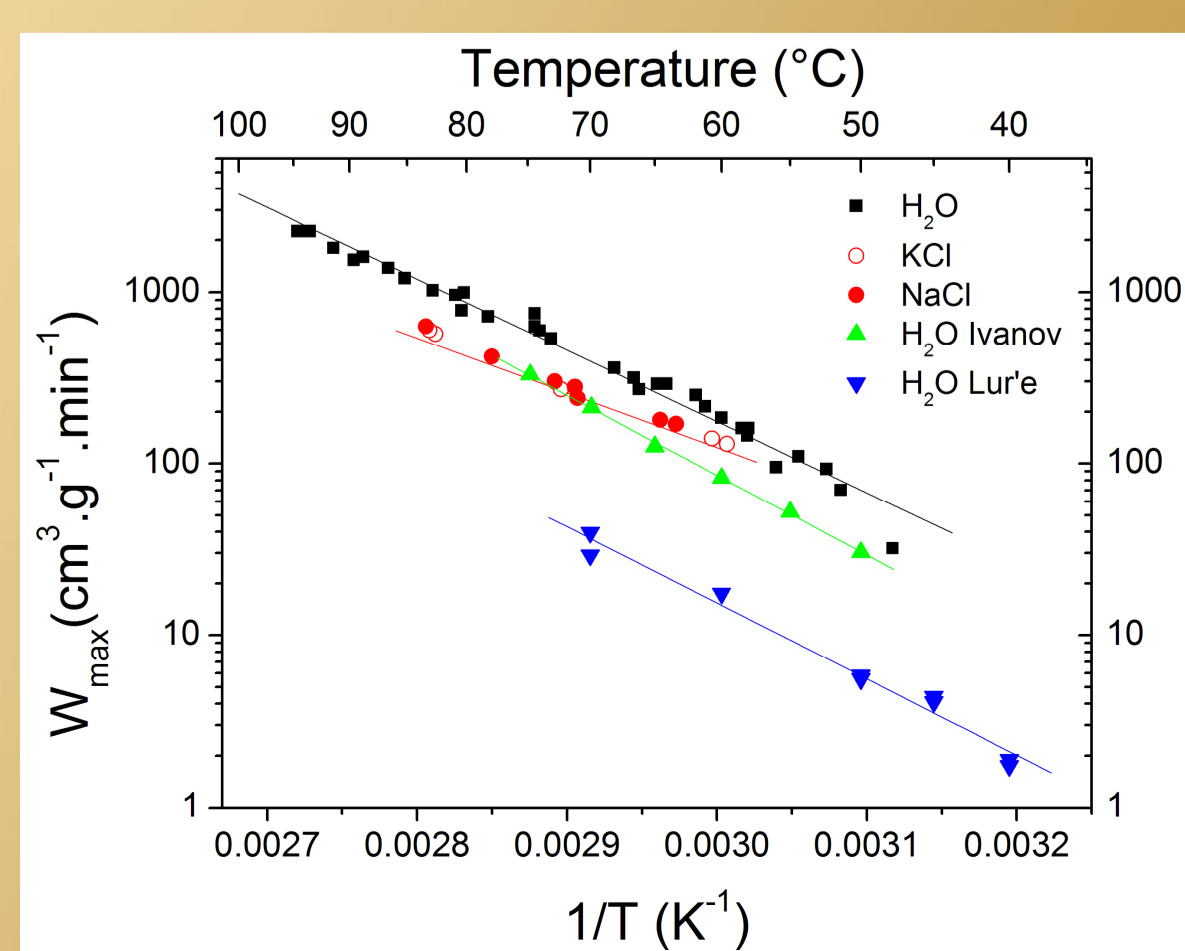
- Temperature dependence of the induction period.
- Rat'ko et al [2] suggest that this induction period corresponds to the hydration of the natural oxide film (Al₂O₃).
- The theoretical value of maximum gas release (1350 cm³ H₂/g Al) is not reached, but conversion is quasi-complete.

- Induction time and maximal flow rate follow an Arrhenius law.
- t_{ind} for saline solutions are higher than for pure water, with lower W_{max} .



$$t_{ind} = t_{ind}^{\infty} \cdot \exp\left(\frac{-E_a}{RT}\right)$$

Solution	t_{ind}^{∞} (s)	E_a (kJ/mol)
H ₂ O	$6.41 \cdot 10^{-11}$	-79.9 ± 4.1
NaCl, KCl solutions	$1.12 \cdot 10^{-10}$	-80.4 ± 4.3

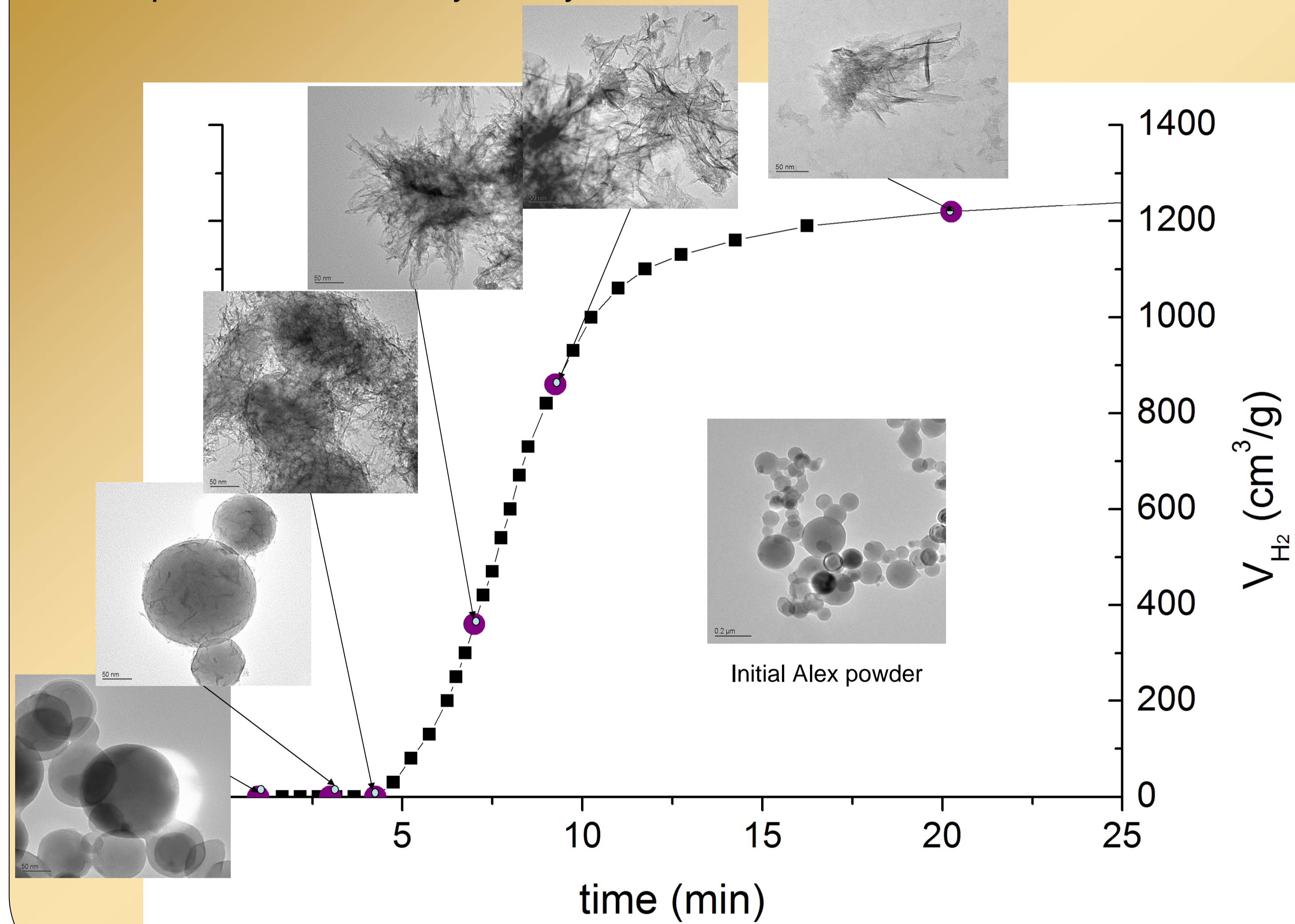


$$W_{max} = W_{max}^{\infty} \cdot \exp\left(\frac{-E_a}{RT}\right)$$

Solution	W_{max}^{∞} (cm ³ /g/min)	E_a (kJ/mol)
H ₂ O, present work	$1.90 \cdot 10^{14}$	77 ± 1.5
H ₂ O, Ivanov <i>et al.</i> [1]	$7.93 \cdot 10^{15}$	89 ± 1.5
H ₂ O, Lur'e <i>et al.</i> [3]	$3.02 \cdot 10^{14}$	85 ± 4.3
NaCl, KCl solutions, present work	$7.70 \cdot 10^{11}$	62 ± 3.5

5 - TEM Analysis

- Quenching of the reaction by freezing mixture samples at different times.
- Samples are then analyzed by TEM.



6 - Conclusions

- The temperature dependence and the influence of salinity have been investigated on the low temperature reactivity of aluminum nanoparticles with water.
- The production of hydrogen is preceded by an induction period corresponding to the hydration-dissolution-precipitation of the oxide film initially covering the particles.
- This induction period is thermally activated ($E_a = -80$ kJ/mol).
- The hydrogen released by the reaction (hydroxidation) is characterized by W_{max} , which is also thermally activated with similar values of E_a found in the literature.
- The hydroxidation of the nanopowder is slowed down in the presence of chloride ions.

References

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