

Methods for measuring hydrogen
in zirconium alloys used in
Studsvik

Anne-Charlotte Nystrand
David Schrire

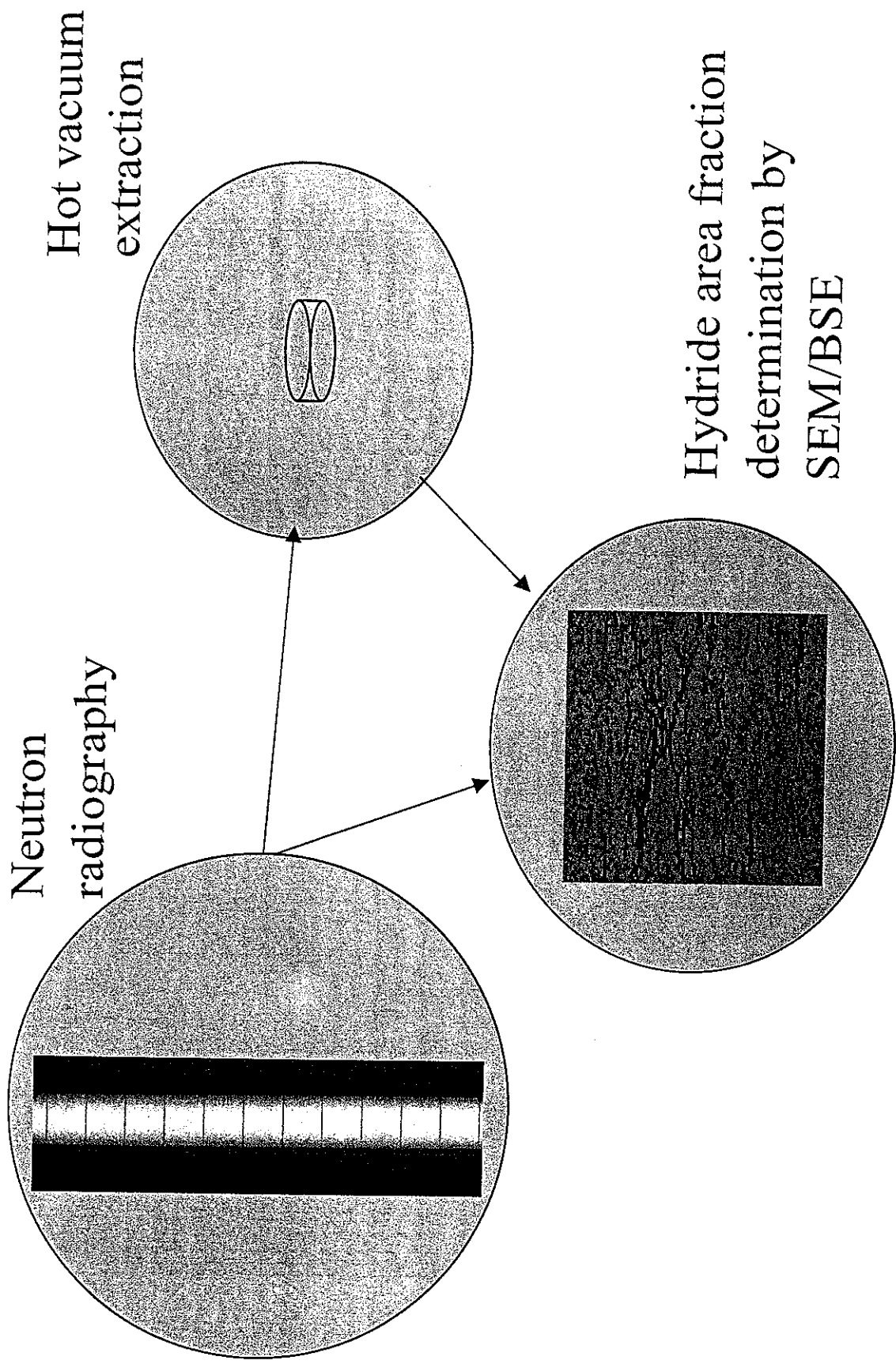
Contents

- Purpose of hydrogen characterisation
- hot vacuum extraction method
 - procedure
 - accuracy/artefacts
- hydride area fraction measurements in SEM/BSE
 - procedure
 - accuracy/artefacts
- comparison with the two methods

Hydrogen uptake in fuel cladding/channels can influence

- Mechanical behavior
- Corrosion behavior
- fuel rod/channel length

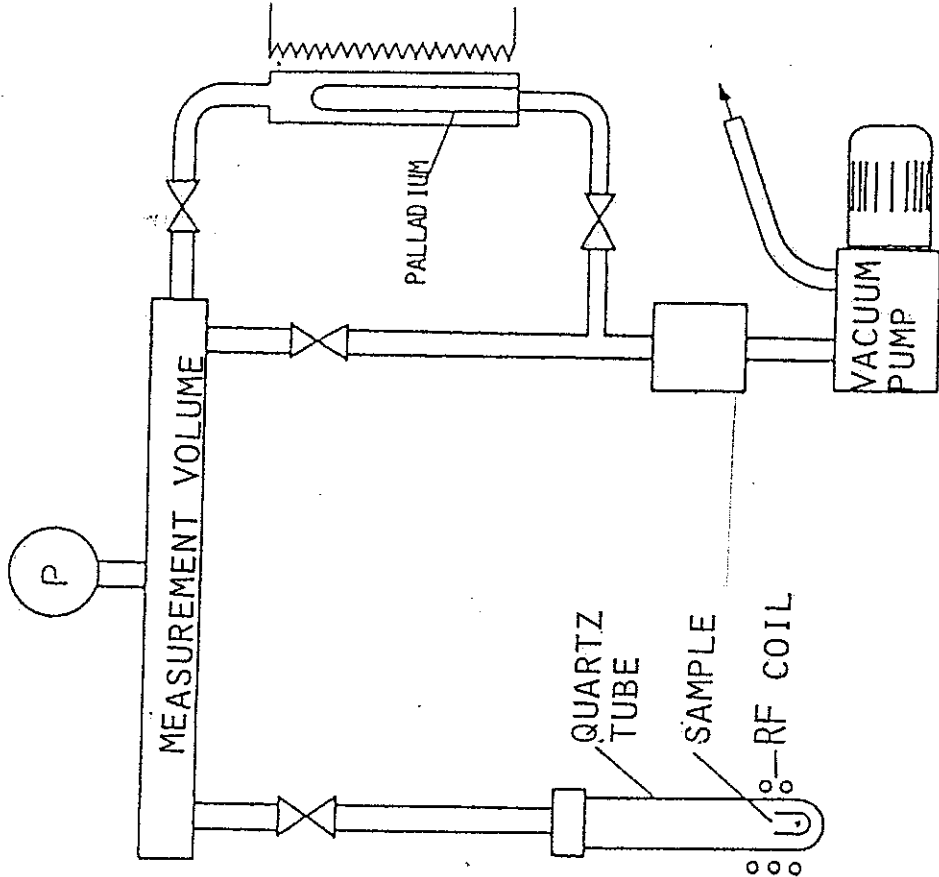
Hydrogen characterisation



Equipment for hot vacuum extraction, HVE (ASTM standard E146-83)

- hydrogen content determined from the volume and the pressure of the gas
- vacuum system
- induction heating of sample in a quartz tube
- calibrated measuring volume
- diaphragm type of gauge for pressure measurements (0-10 mbar)
- evacuation via diffusion through palladium filter

Equipment for HVE



Procedure for HVE of hydrogen in fuel cladding

- Sample preparation
 - 1-mm thick cladding rings (50-100 mg)
 - defueling
 - cleaning
 - weighing
- hydrogen measurements
 - outgassing/calibration at 1300 °C, without sample
 - hydrogen extraction from cladding at 1300 °C

Estimation of uncertainty in hydrogen determination by HVE

- Uncertainty of volume and pressure
- uncertainty of residual hydrogen gas in the sample chamber
- slight absorption of hydrogen by crucible material
- uncertainty of expected hydrogen remaining in the sample
- error, ≤ 50 ppm for 1000 ppm, 100 mg

A comparison

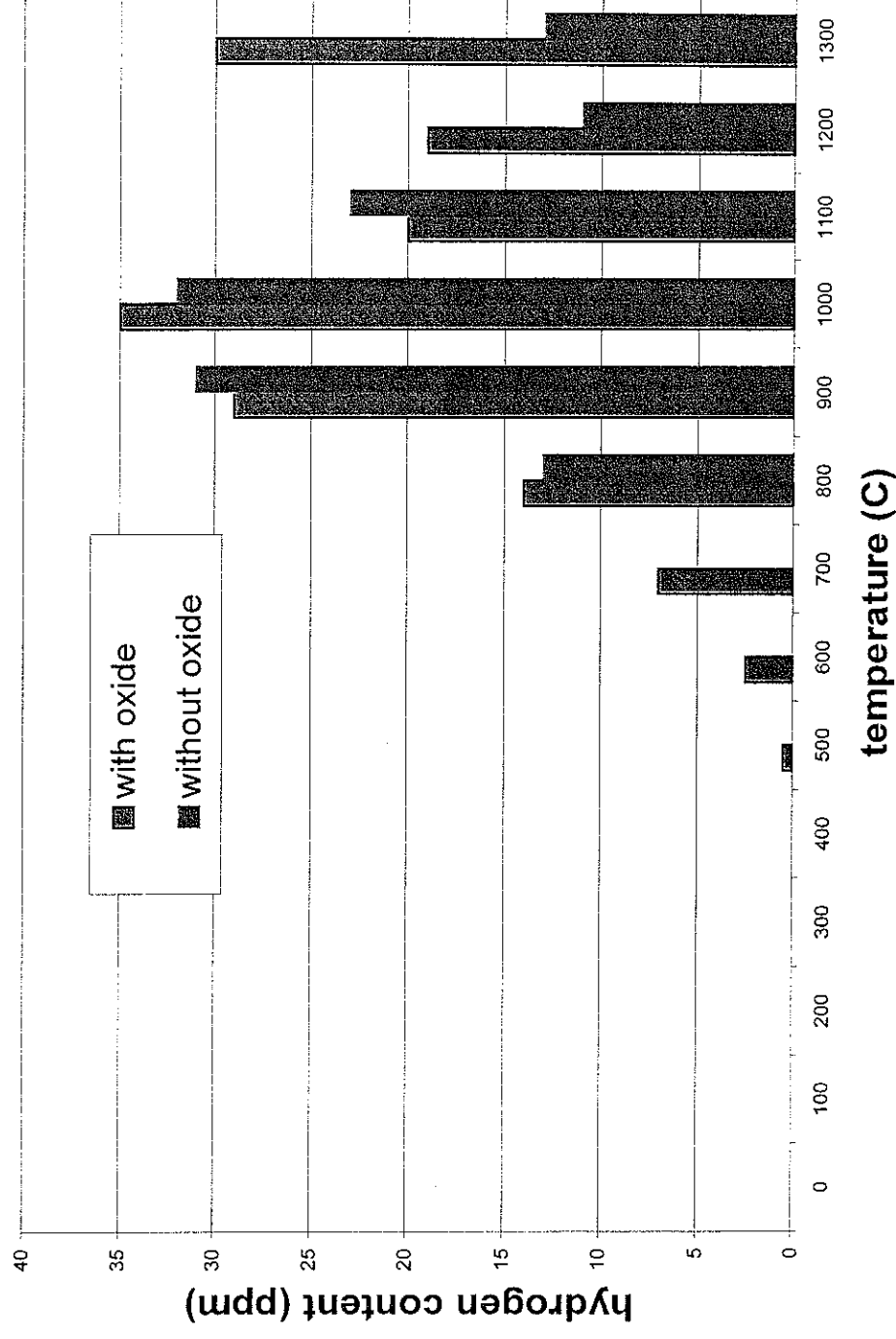
Sample identification	AECL Chalk River	AECL Whiteshell	Studsvik
B6 (A)	305	304	297
A1 (A)	716	735	722
A11 (A)	1075	987	975

Errors from sample when using

HVE

- hydrogen may be extracted from the oxide on the fuel cladding/channel
- fission product gas may be released from the inner fuel cladding surface

Extracted hydrogen from fuel channel samples as a function of temperature



The results of hot extraction experiments made on a piece of Zry sample, oxide powder and their mixture.

	Weight (g)	Pressure (mbar)	Extracted H (μg)
Zry	0.0241	0.19	1.8
Oxide	0.2500	1.54 [¶] →1.52 [§]	0
Zry + oxide	0.0277 _{Me} + 0.1356 _{Ox}	1.54 [¶] →0.47 [§]	9.4 _{obs} , 10.5 _{calc} [#]

[¶] measured after two minutes of hot extraction.

[§] measured after 12 minutes of hot extraction.

[#] the calculation was based on the assumption that water vapor releases from the oxide and completely reacts with Zry metal.

Procedure for hydride measurements by SEM in backscatter mode (BSE)

- Sample preparation
 - thin defueled cladding ring etc
 - mounting, grinding, polishing, conductive coating
- hydrogen measurements
 - based on backscattered electron imaging exploiting atomic number contrast
 - radial scan of images to cover the wall thickness in SEM/BSE
 - images digitized and analyzed by image analysis system

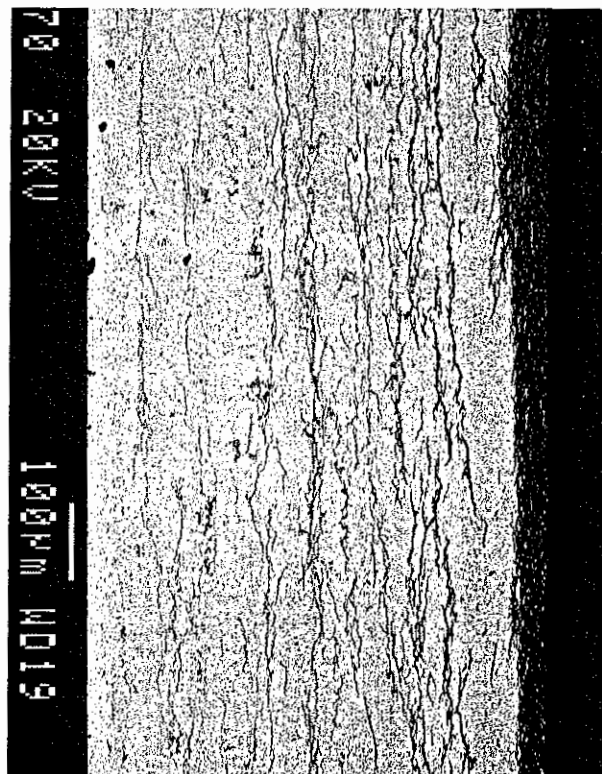
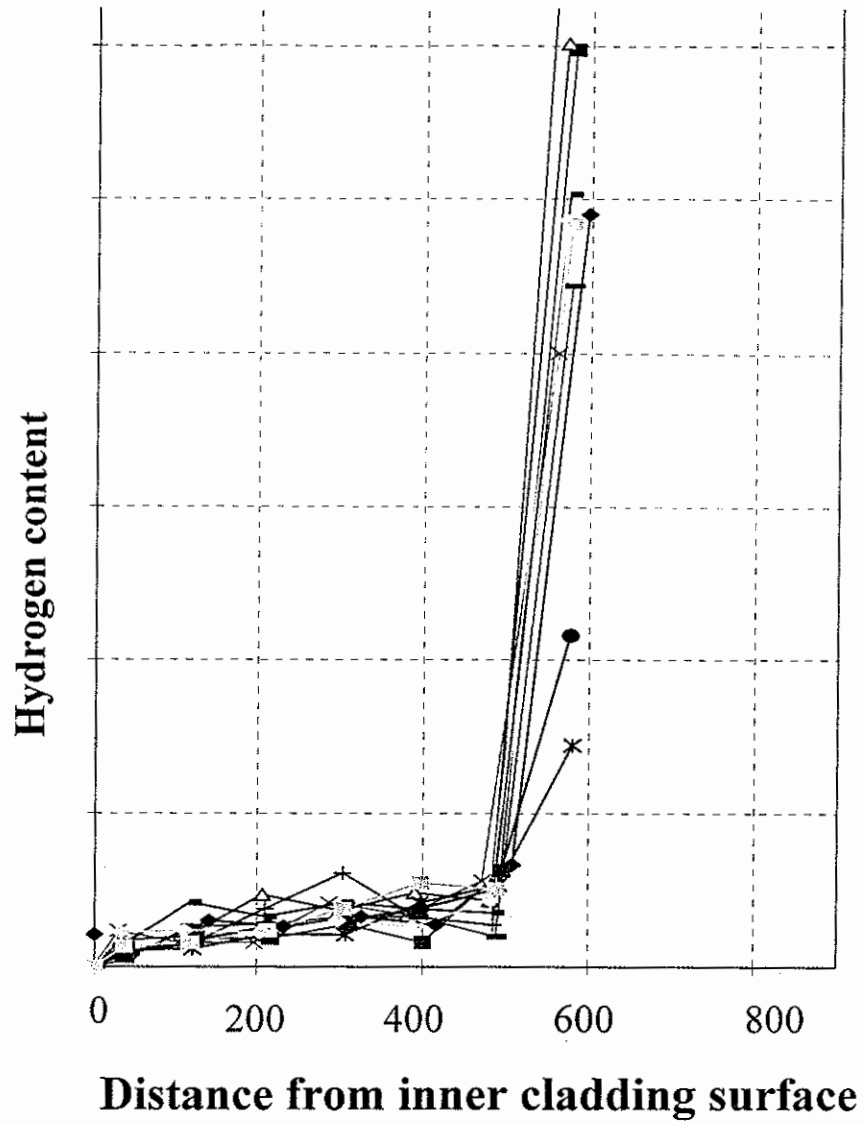
Assumptions for hydrogen determination by SEM/BSE

- Hydrided material has been cooled slowly (in-reactor or furnace-cooled)
- all the hydrides are of the δ phase
- hydride area fraction = hydride volume fraction

Relationship between hydrogen concentration and hydride are fraction

$$Wt_h = Wt_\delta \cdot F \left(\frac{\rho_\delta}{\rho_{Zr}(1-F) + \rho_\delta \cdot F} \right)$$

- $Wt_H =$ wt ppm H
- $Wt_\delta =$ wt ppm H in δ -phase hydride (17570 ppm)
- $F =$ measured hydride area (volume) fraction
- $\rho_\delta =$ density of δ -phase hydride (5,65 g/cm³, RT)
- $\rho_{Zr} =$ density of α -phase metal (6,54 g/cm³, RT)



Experimental errors in hydrogen measurements by SEM/BSE

- Preparation artefacts
- Incorrect threshold setting
- Instrument drift and sample shading
- depth of information
- hydride phase composition and density
- hydride heterogeneity

HVE versus SEM hydrogen

