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**Joint ICTP/IAEA Workshop on Irradiation-induced Embrittlement of  
Pressure Vessel Steels**

*23 - 27 November 2009*

**Ageing phenomena in RPV materials**

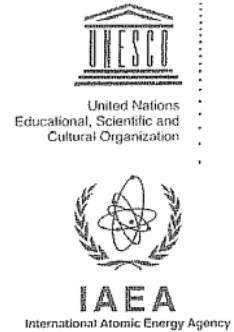
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# AGEING PHENOMENA IN RPV MATERIALS

**Milan Brumovský**

**Joint ICTP/IAEA Workshop on Effects of Mechanical  
Properties and Mechanisms Governing the Irradiation-  
induced Embrittlement of Pressure Vessel Steels  
23 - 27 November 2009**



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- THERMAL AGEING
- TEMPER EMBRITTLEMENT
- FATIGUE
- CORROSION
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- CONCLUSIONS



# DEFINITIONS

- **AGEING** is a general process where the characteristics of **SSCs\*** change with time
- **AGEING DEGRADATION** is where ageing effects reduce or impair the ability of **SSCs** to function within acceptance criteria
- **AGEING MANAGEMENT** relates to engineering operations and maintenance activities aimed at controlling ageing degradation within acceptable limits.
- **SSCs**- Systems, Structures and Components



# DEFINITIONS

- Degradation is a deterioration phenomenon which might lead to component failure or limit the life of a component or power plant. Ageing describes a continuous time or operational degradation of materials due to operating conditions, which include normal and operating conditions (but excludes 'design' and 'beyond design basis' accidents). As a result of ageing degradation the plant or component state could vary through the operating life.



# DEFINITIONS

All components of NPP are subject to ageing. However the rates and significance of degradation, and therefore component lifetimes, vary considerably. Ageing may lead to the degradation of physical barriers and redundant components resulting in an increased probability of common cause failures. It is possible that degradation not revealed during normal operation and testing could lead to failures.



# DEFINITIONS

All components 'age', but it is the rate of degradation and its significance that determines its importance with regard to failure. While the following is not an exhaustive exposition we have again taken metallic materials of key component materials as an example, where the main degradation mechanisms include metallurgical phenomena such as irradiation embrittlement, fatigue, corrosion, interaction of mechanisms and so on.





# DEFINITIONS

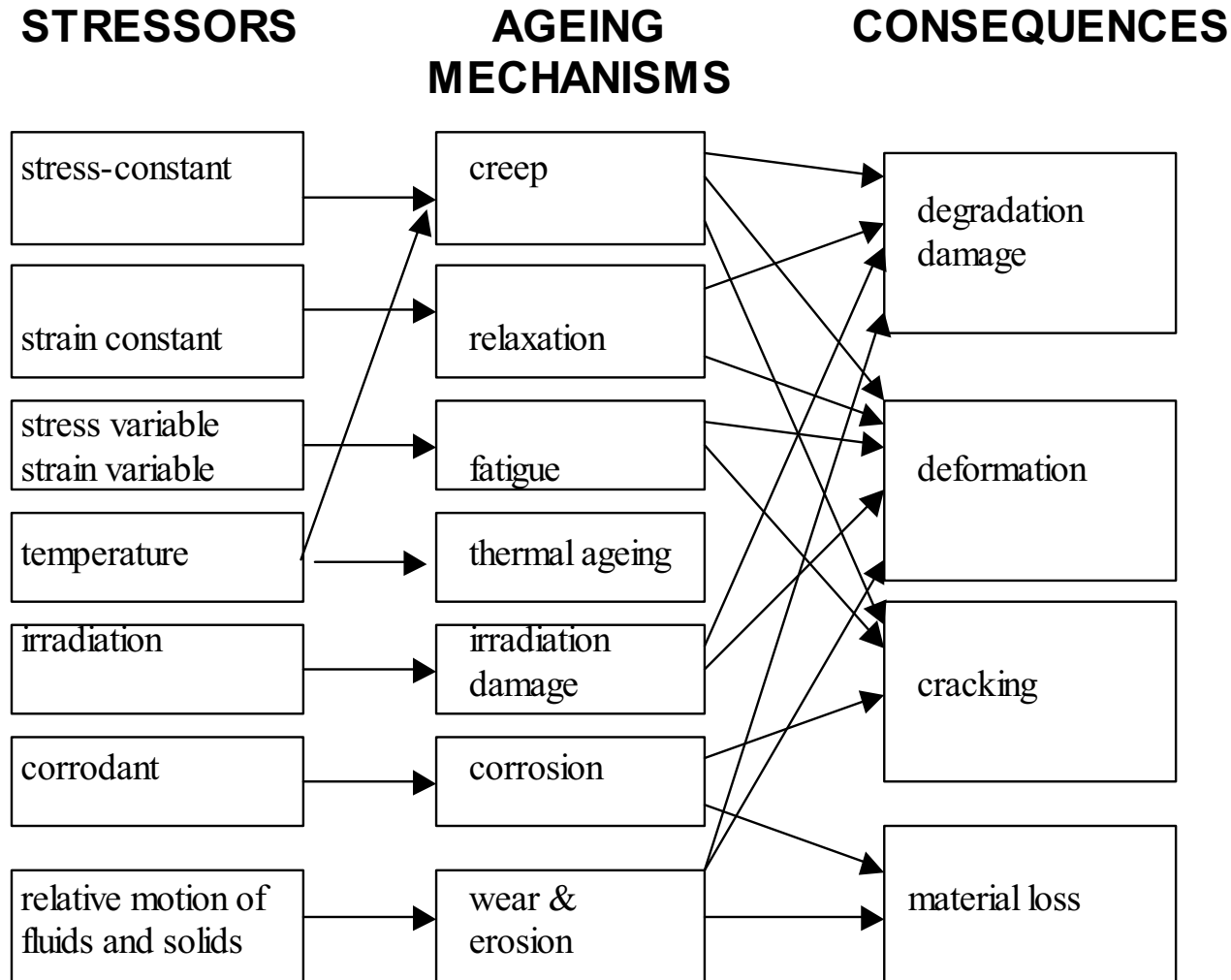
Ageing degradation mechanisms are usually classified into categories, which can be subdivided into those which:

- affect the internal microstructure or chemical composition of the material and thereby change its intrinsic properties (thermal ageing, creep, irradiation etc.),
- impose physical damage on the component either by metal loss (corrosion, wear) or by cracking or deformation (stress-corrosion, deformation or cracking).





# DEFINITIONS



*Ageing factors, basic ageing mechanisms and possible consequences. A major stressor in an ageing structure is time itself. (For example, in the embrittlement of rubber and plastic materials in components)*



# DEFINITIONS

	Irradiation	Thermal ageing	Creep	Fatigue	Corrosion Fatigue	Stress corr <sup>n</sup> cracking	Strain induced corr <sup>n</sup> cracking	Intergranular attack	Erosion corr <sup>n</sup>	Local corr <sup>n</sup> attack	General Corr <sup>n</sup>	Wear
Change of Material properties	x	x	x	x								
Cracking	x		x	x	x	x	x					x
Dimensional changes	x		x									
Wall thickness									x	x	x	
Denting										x		
Pitting												x

*Potential ageing mechanisms and resulting effects on component*



# DEFINITIONS

- The technical evaluation of a particular age-related degradation mechanism and its effects on the continued safety or functional performance of a particular PWR RPV component leads to one of two conclusions:
  - (1) **the degradation mechanism effects** are potentially significant to that component and further evaluation is required relative to the capability of programmes to effectively manage these effects;



# DEFINITIONS

- or (2) **the age-related degradation effects are not significant** to the ability of that component to perform its intended safety function throughout the remainder of plant life. For the latter case, specific criteria and corresponding justification are provided. These criteria can be used as the basis for generic resolution of age-related degradation mechanism/component issues.



# DEGRADATION MECHANISMS

The set of age-related degradation mechanisms is derived from a review and evaluation of relevant operating experience and research. This set consists of the following mechanisms:

1. Radiation Embrittlement
2. Thermal Ageing
3. Temper Embrittlement
4. Fatigue
5. Corrosion
  - Intergranular attack and PWSCC of Alloy 600 components, Alloy 82/182 welds, radial keys, etc.
  - General Corrosion and pitting
  - Boric acid corrosion
6. Wear



# RADIATION EMBRITTLEMENT

- The degree of embrittlement and hardening induced in ferritic steels after exposure to fast neutron radiation is an issue of the utmost importance in the design and operation of NPPs. The area of the RPV surrounding the core (called the beltline region) is the most critical region of the primary pressure boundary system because it is subjected to significant fast neutron bombardment. The overall effect of fast neutron exposure is that ferritic steels experience an increase in hardness and tensile properties and a decrease in ductility and toughness, under certain conditions of radiation.





# RADIATION EMBRITTLEMENT

- The effect of neutron fluence on radiation hardening and embrittlement has been reported to be significant at fluences above  $10^{22} \text{ m}^{-2}$  ( $E > 1 \text{ MeV}$  for LWR and  $E > 0.5 \text{ MeV}$  for WWER ). Unless a steady state or saturation condition is reached, an increase in neutron fluence results in an increase in RTNDT/ $T_k$ , yield strength and hardness, and a decrease in the Charpy toughness, also in the upper shelf temperature region. There are significant variations in the fluence and radiation damage around the circumference and in the longitudinal direction of RPVs.





# RADIATION EMBRITTLEMENT

- Alloy composition, (especially when consideration is given to impurity copper and phosphorus and alloying element nickel) is known to have a strong effect on radiation sensitivity. Data have been generated on both commercial and model alloys to show the effects of alloy composition.



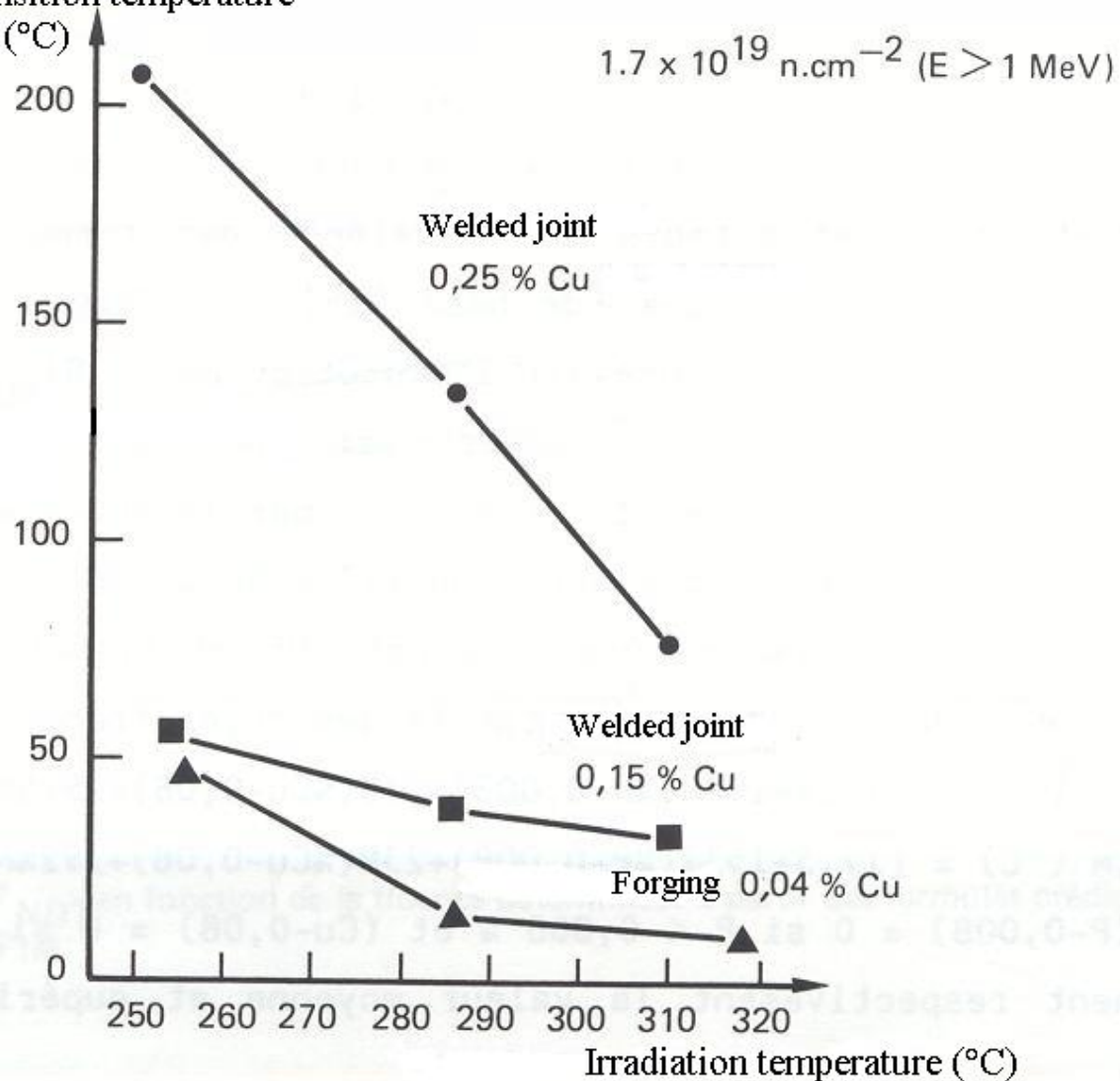
# RADIATION EMBRITTLEMENT

- Radiation temperature has long been recognized to have an effect on the extent of the radiation damage. Data from the early nineteen-sixties demonstrated that the maximum embrittlement occurred during radiation at temperatures below  $120^{\circ}\text{C}$  ( $250^{\circ}\text{F}$ ). Recent studies have reported a decrease in radiation embrittlement at higher temperatures ( $>310^{\circ}\text{C}$ ), which is attributed to the dynamic in-situ "annealing" of the damage.



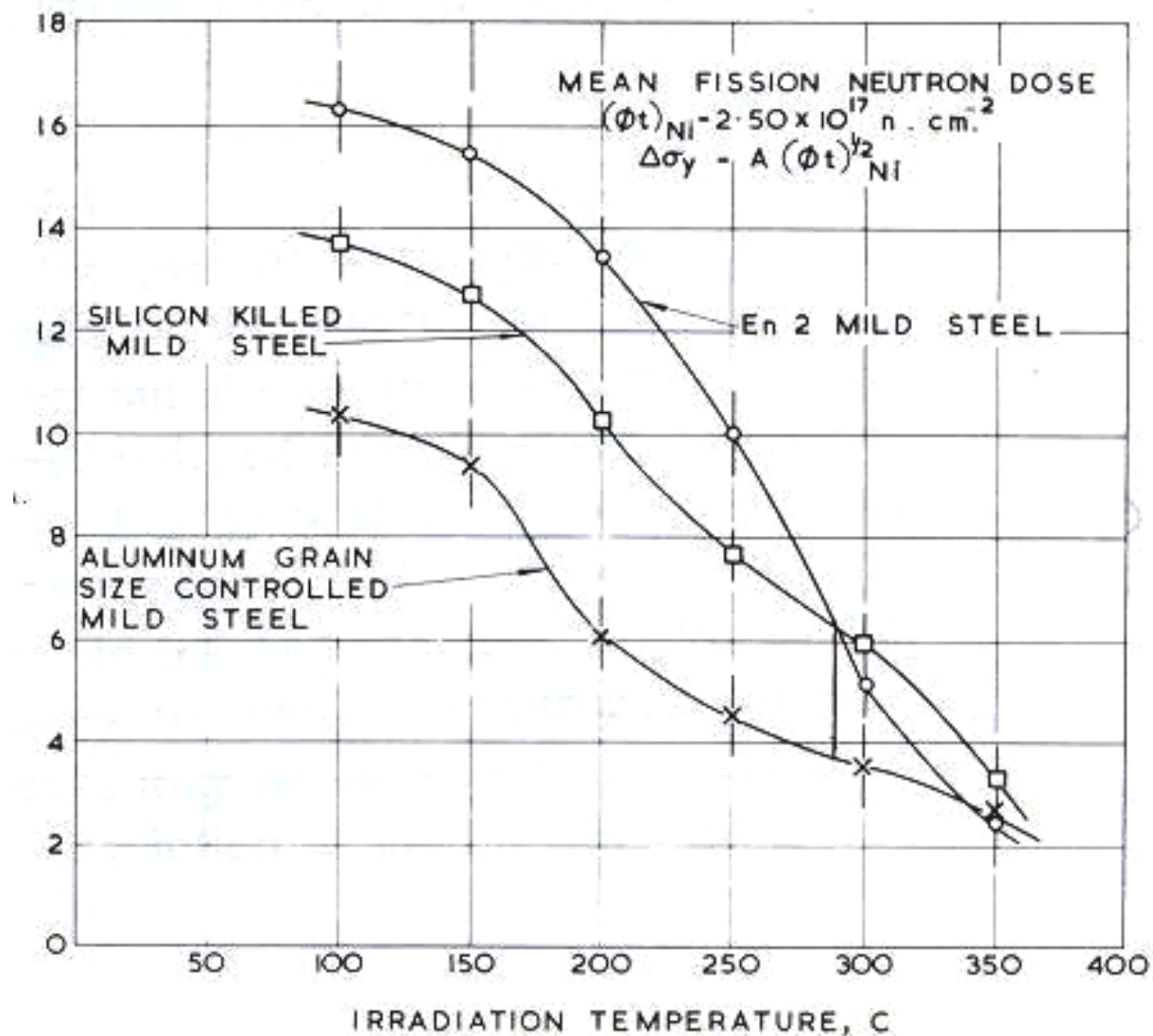
# RADIATION EMBRITTLEMENT

Shift of the Charpy transition temperature  
measured at 41 Joules (°C)





# RADIATION EMBRITTLEMENT





# RADIATION EMBRITTLEMENT

## □ EFFECT OF IRRADIATION TEMPERATURE IN CODE PREDICTIVE FORMULAE

- $\Delta RT_{NDT} = A(\text{Chemical Composition, Irradiation Temp., Flux})\Phi^n + \text{Constant}$
- The general expression of  $\Delta RT_{NDT}$  may be reduced to the following:
- $\Delta RT_{NDT} = CF \cdot FF$
- In the case of the Russian standard, the expressions are generally as follows:

$$\Delta T_K = A_F \cdot \left( \frac{F}{10^{22}} \right)^{\frac{1}{3}}$$



# RADIATION EMBRITTLEMENT

MATERIAL		IRRADIATION TEMPERATURE $T_{IRR}$ , [°C]	IRRADIATION EMBRITTLEMENT COEFFICIENT $A_F$ , [°C]
15Kh2MFA	BASE METAL	250	22
		270	18
		290	14
	A/S WELD METAL	250	$800(P+0.07 Cu)+8$
		270	$800(P+0.07 Cu)$
15Kh2MFA-A	BASE METAL	270	12
		290	9
	A/S WELD METAL	270	15
		290	12





# RADIATION EMBRITTLEMENT

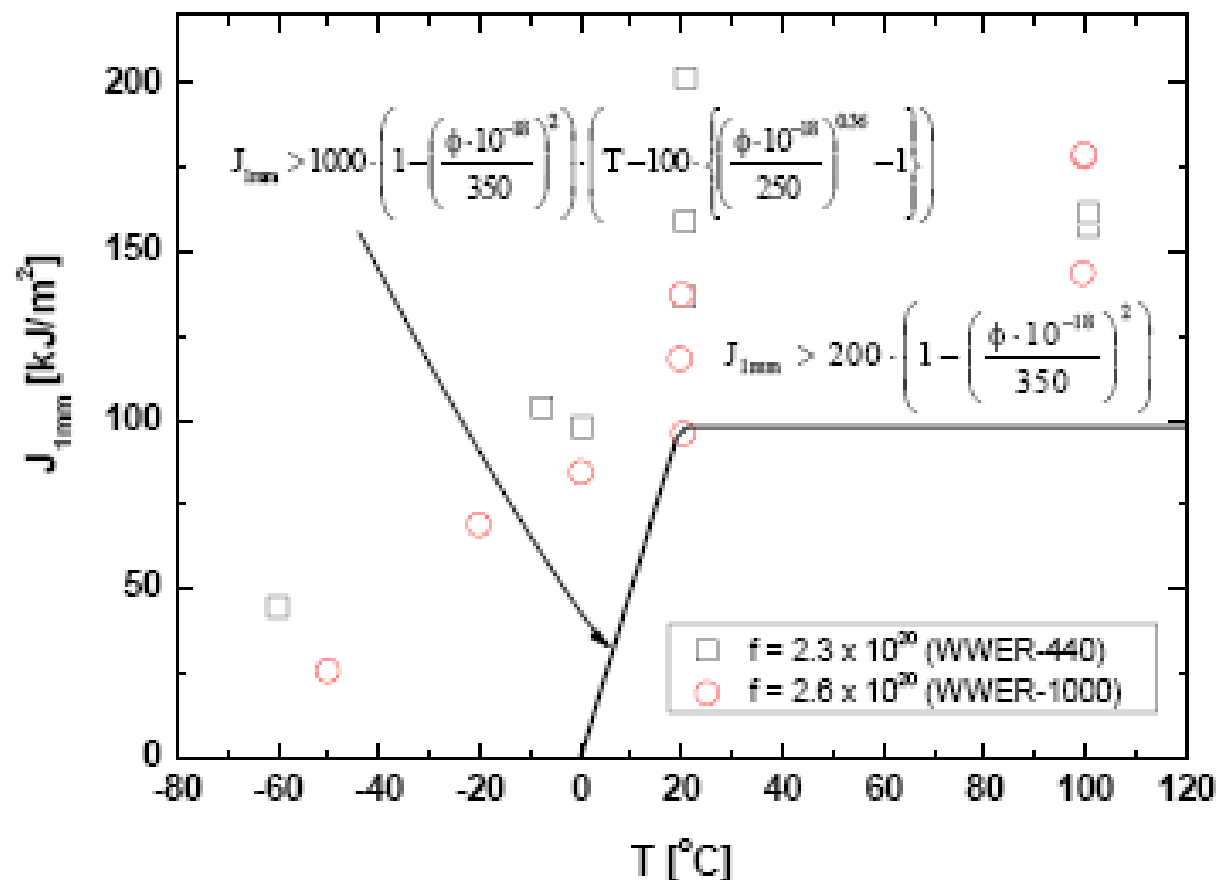
The expression developed by the NRC for the prediction of  $\Delta RT_{NDT}$  ( $\Delta T_{41J}$ ) is:

$$\Delta RT_{NDT} = A \cdot \exp\left(\frac{1.930 \times 10^4}{T_c + 460}\right) \cdot (1 + 110 \cdot P) \cdot f(\phi \cdot t) \quad (5.5)$$
$$+ B \cdot (1 + 2.40 \cdot Ni^{1.25}) \cdot h(Cu) \cdot g(\phi \cdot t) + BIAS$$



# RADIATION EMBRITTLEMENT

Fig.5.6. Combination of VTT analysis with Prometey data enables estimation of lower bound tearing resistance of WWER cladding materials as a function of temperature and fluence.





# ANNEALING

- ❑ Effective process for initial material properties restoration
- ❑ Two different procedures:
- ❑ Re-embrittlement process - under study
  - Wet annealing limited by reactor design parameters and water limiting conditions, i.e. up to approx. 320 °C - less effective
  - Dry annealing - effectiveness up to 90-100 %, effective when annealing temperature is higher by about 150-200 °C over operation temperature
  - standard regimes - 450-475 °C - 100-168 hours
- ❑ Re-embrittlement process - under study



# RADIATION INDUCED CREEP, RELAXATION AND SWELLING

- ❑ Neutron irradiation creates a large number of interstitials and vacancies that can annihilate on sinks such as dislocations, grain boundaries, surfaces, etc. by diffusion controlled processes. The kinetics of annihilation are different for interstitials and vacancies and depend on stress, temperature, material microstructure, etc.
- ❑ If interstitials are eliminated rapidly, the excess vacancies coalesce into voids or bubbles inside the metal leading to swelling of the structure
- ❑ **THIS MECHANISM CAN BE IMPORTANT FOR REACTOR INTERNALS**



# THERMAL AGEING

- Thermal ageing is a temperature, material state (microstructure), and time dependent degradation mechanism. The material may lose ductility and become brittle because of very small microstructural changes in the form of precipitates coming out of solid solution. In the case of RPV steel with impurity copper, the important precipitates are copper-rich (however, there could be other precipitates). The precipitates block dislocation movement thereby causing hardening and embrittlement. The impurity copper in RPV steel is initially trapped in solution in a super-saturated state.



# THERMAL AGEING

- With time at normal PWR operating temperatures ( $\sim 290^{\circ}\text{C}$ ), it may be ejected to form stable precipitates as the alloy strives toward a more thermodynamically stable state, even if there is no radiation damage.



# THERMAL AGEING

- ❑ Susceptible to this kind of mechanisms are cast stainless steels, to a lesser extent weld metal and some Cr rich martensitic steels
- ❑ Thermal ageing embrittlement of cast duplex stainless steel at these temperatures can cause an increase in the hardness and tensile strength and a decrease in ductility, impact strength and fracture toughness of the material.





# THERMAL AGEING

- Transition temperature shift due to thermal ageing is defined as

$$\Delta T_T = T_{kT} - T_{k0}$$

extrapolation up to 100 000 h :

- monotonous trend

$$\Delta T_T = \Delta T_T^{\text{lim}} [1 - \exp(-pt)]$$

on the basis of experiments with holding times

$t = 500, 1\ 000, 3\ 000, 5\ 000, (7\ 500), 10\ 000$  h





# THERMAL AGEING

## local extreme

$$\Delta TT = \Delta TT_{\max}[-b(t-t_{\max})] + c$$

## extrapolation from higher temperature

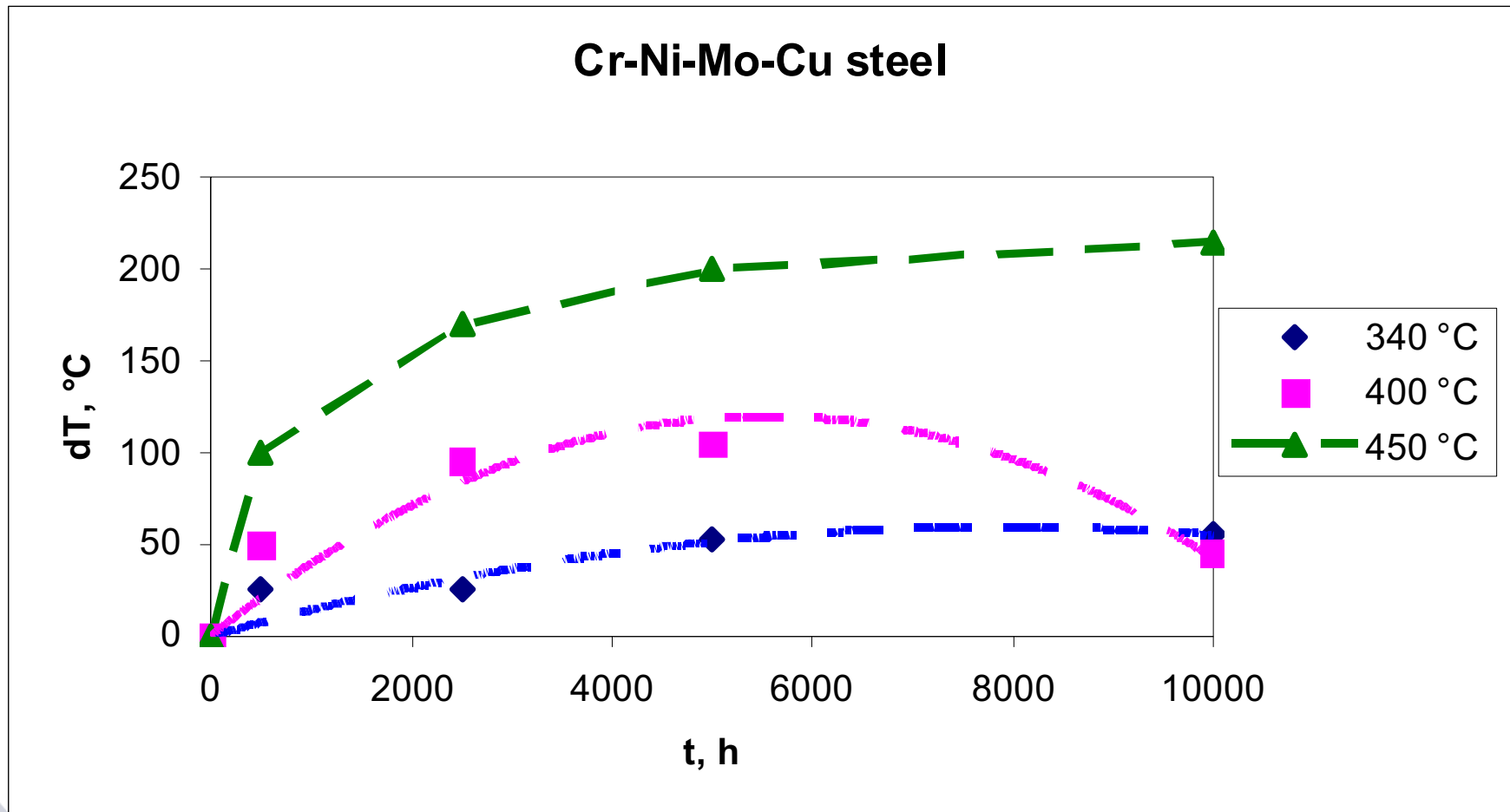
$$H_p = (T+273)(k+\lg t) \cdot 10^{-3}$$

$$k = 8$$

thermal ageing should be performed at  
 $T+50$  °C for 1 000, 3 000 and 5 000 h

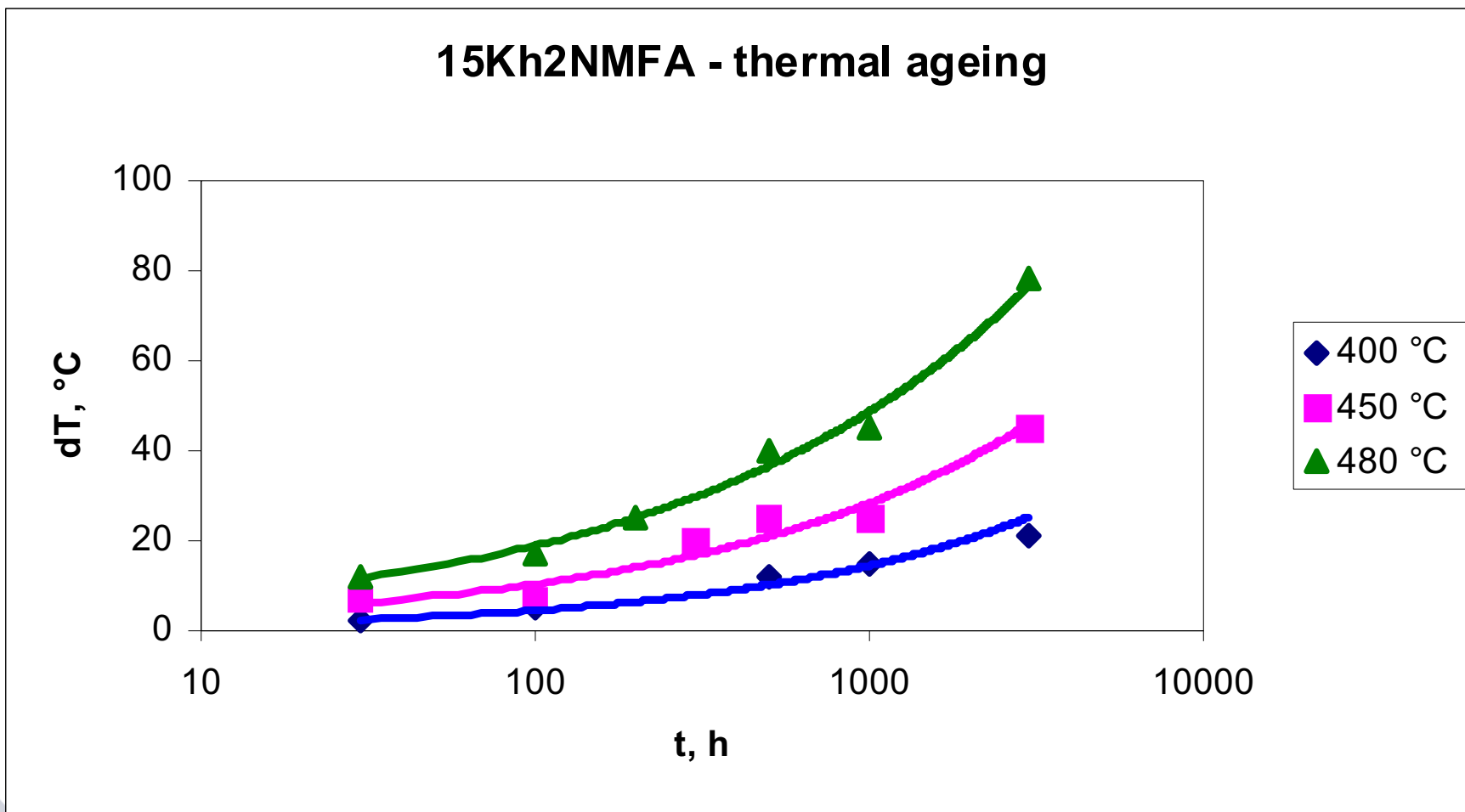


# THERMAL AGEING





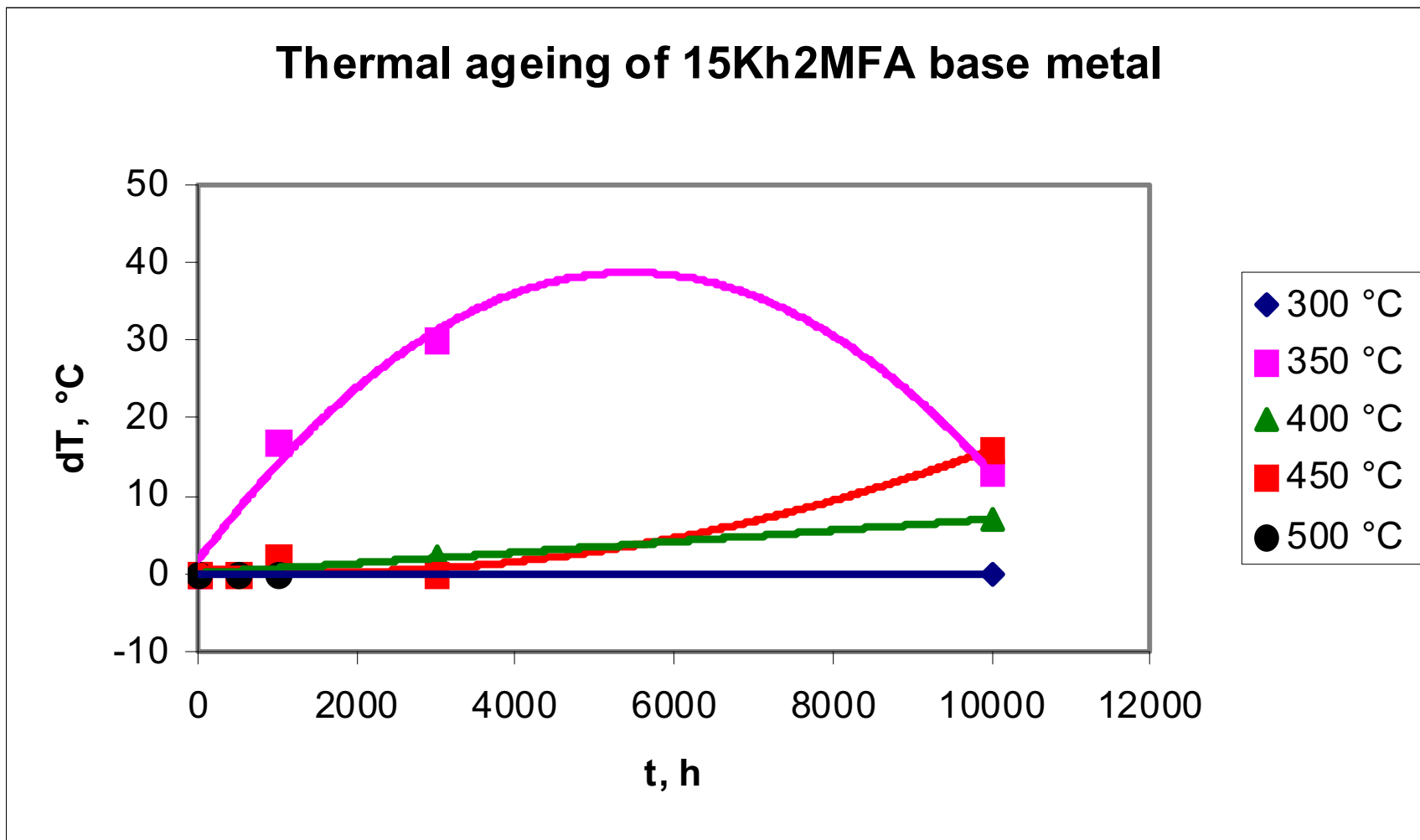
# THERMAL AGEING





# THERMAL AGEING

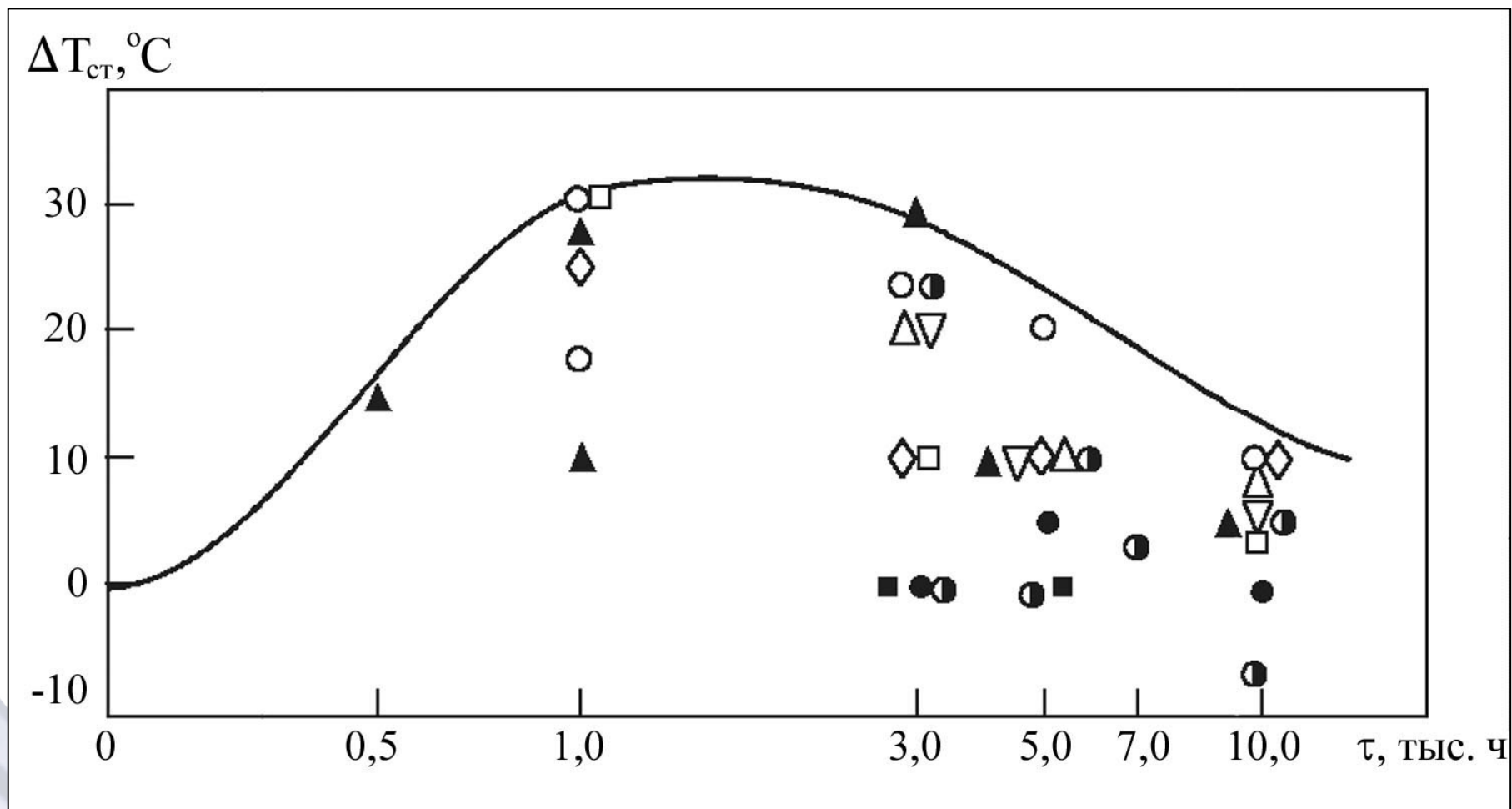
## Thermal ageing of 15Kh2MFA base metal





# THERMAL AGEING

## Thermal ageing of 15Kh2MFA



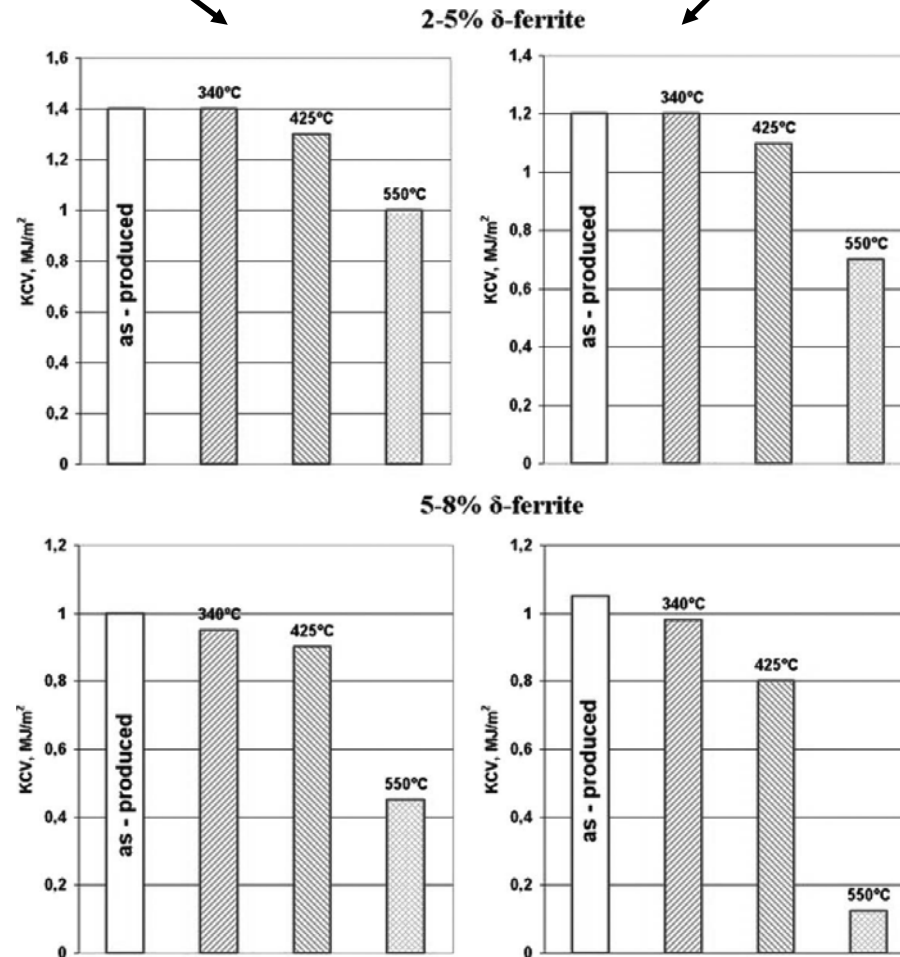


# THERMAL AGEING EFFECT ON IMPACT STRENGTH OF ANTICORROSION CLAD METAL

1ST LAYER – 25/13

10,000 h

2ND LAYER – 18/10 Nb





# THERMAL AGEING

- ❑ - WWER RPV steels are relatively well stable against thermal ageing at 350 °C
- ❑ - transition temperature shift near this temperature exhibits local maximum for holding times between 1000 and 10 000 h
- ❑ - WWER Code gives guaranteed transition temperature shifts for 350 °C and 100 000 h
- ❑ - WWER reactors (V-440/213 and V-1000/320) contain in RPV surveillance specimens programme also specimens for thermal ageing determination
- ❑ PWR Codes do not contain any data on thermal ageing of RPV materials even though these steels are also susceptible to some degradation by this mechanism





# TEMPER EMBRITTLEMENT

- However, the effect of phosphorus in weld metals and the heat affected zones is of concern, particularly when a thermal annealing may be applied to restore toughness. The propensity of phosphorus to migrate to grain boundaries in the RPV materials and thereby cause embrittlement under certain thermal conditions should be accounted for.



# TEMPER EMBRITTLEMENT

- RPV steels with phosphorus content well above about 0.02 wt% may be susceptible to temper embrittlement during fabrication. However, the Western RPV materials normally contained less than 0.020 wt% phosphorus. Therefore, it is unlikely that any Western RPVs will exhibit temper embrittlement. If a 500°C and higher temperature of thermal anneal of an irradiated RPV is required for recovery of the fracture toughness, the possibility of temper embrittlement should be evaluated.



# FATIGUE

- Fatigue is defined as the structural deterioration that occurs as a result of repeated stress/strain cycles cause by fluctuating loads and temperatures after repeated cyclic loading of sufficient magnitude microstructural damage can accumulate, leading to macroscopic crack initiation at the most highly affected locations. Subsequent mechanical cyclic loading can lead to growth of the initiated crack.



# FATIGUE

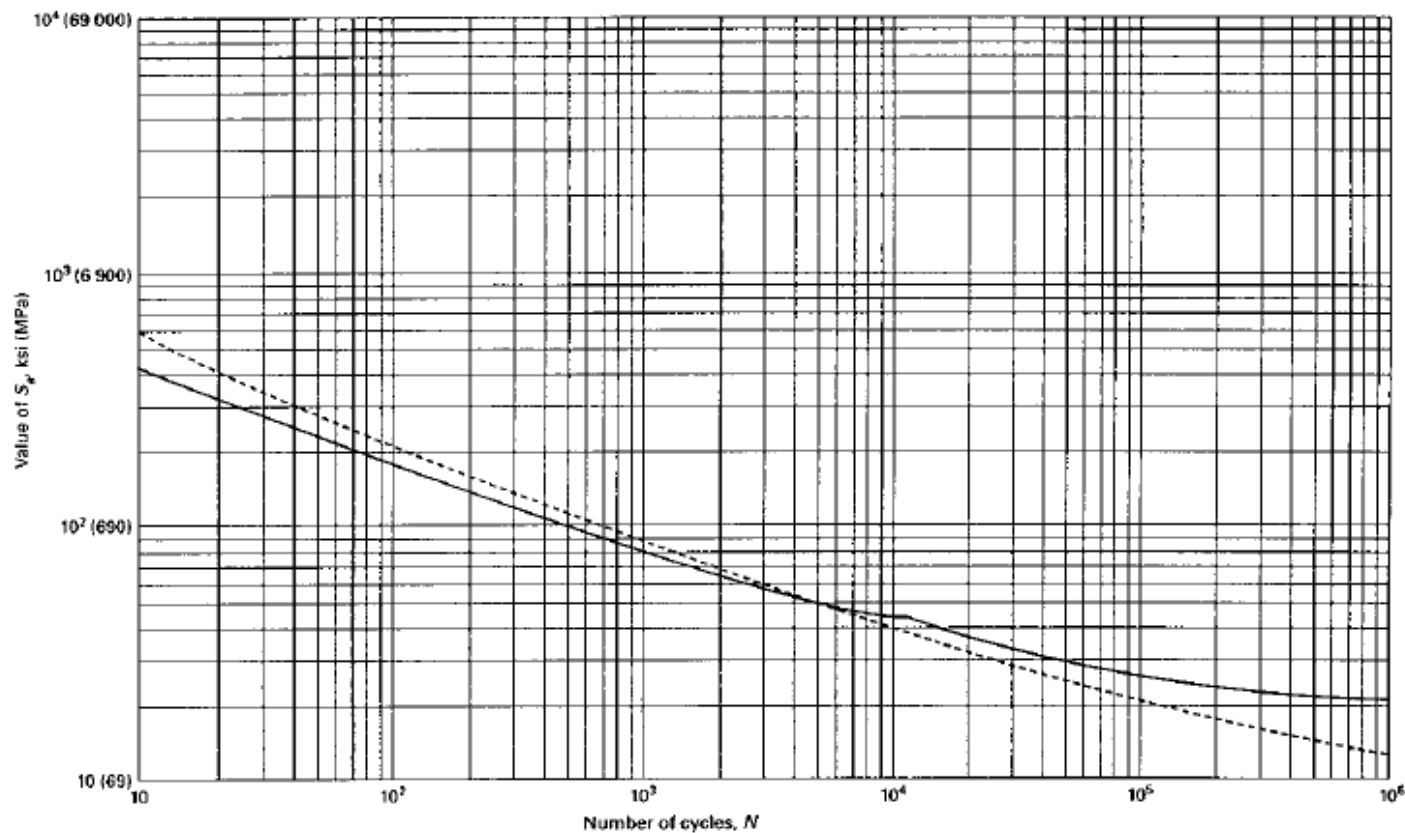
- Fatigue behaviour is related to a variety of parameters, such as stress range, mean stress, cycling frequency, surface roughness and environmental conditions. Cracks initiate at stress concentrations such as geometric notches and surface defects. Fatigue initiation curves indicate how many stress cycles it takes to initiate fatigue cracks in components. These curves are materials related and indicate the allowable number of stress cycles for applied cyclic stress amplitudes.



# FATIGUE

- ❑ Environment can significantly influence fatigue crack initiation. Environmentally assisted fatigue, often referred to as corrosion fatigue, must be considered when dealing with components in the PWR environment.
- ❑ There are three sources of fatigue significant to the PWR. These are system cycling, thermal cycling and flow induced vibration.

# ASME CODE, SECTION III



NOTE:  $E = 30 \times 10^6$  psi (207 MPa)  
 - - - - UTS  $\leq 80.0$  ksi (551 MPa)  
 ——— UTS 115.0 – 130.0 ksi (793 – 830 MPa)  
 Interpolate for UTS 80.0 – 115.0 ksi (551 – 793 MPa)

FIG. I-9.1 DESIGN FATIGUE CURVES FOR CARBON, LOW ALLOY, AND HIGH TENSILE STEELS FOR METAL TEMPERATURES NOT EXCEEDING 700°F

Table I-9.1 Contains Tabulated Values and a Formula for Accurate Interpolation of These Curves

Fig. I-9.1

2001 SECTION III, DIVISION 1 – APPENDICES

6





# PNAE G-7-002-86

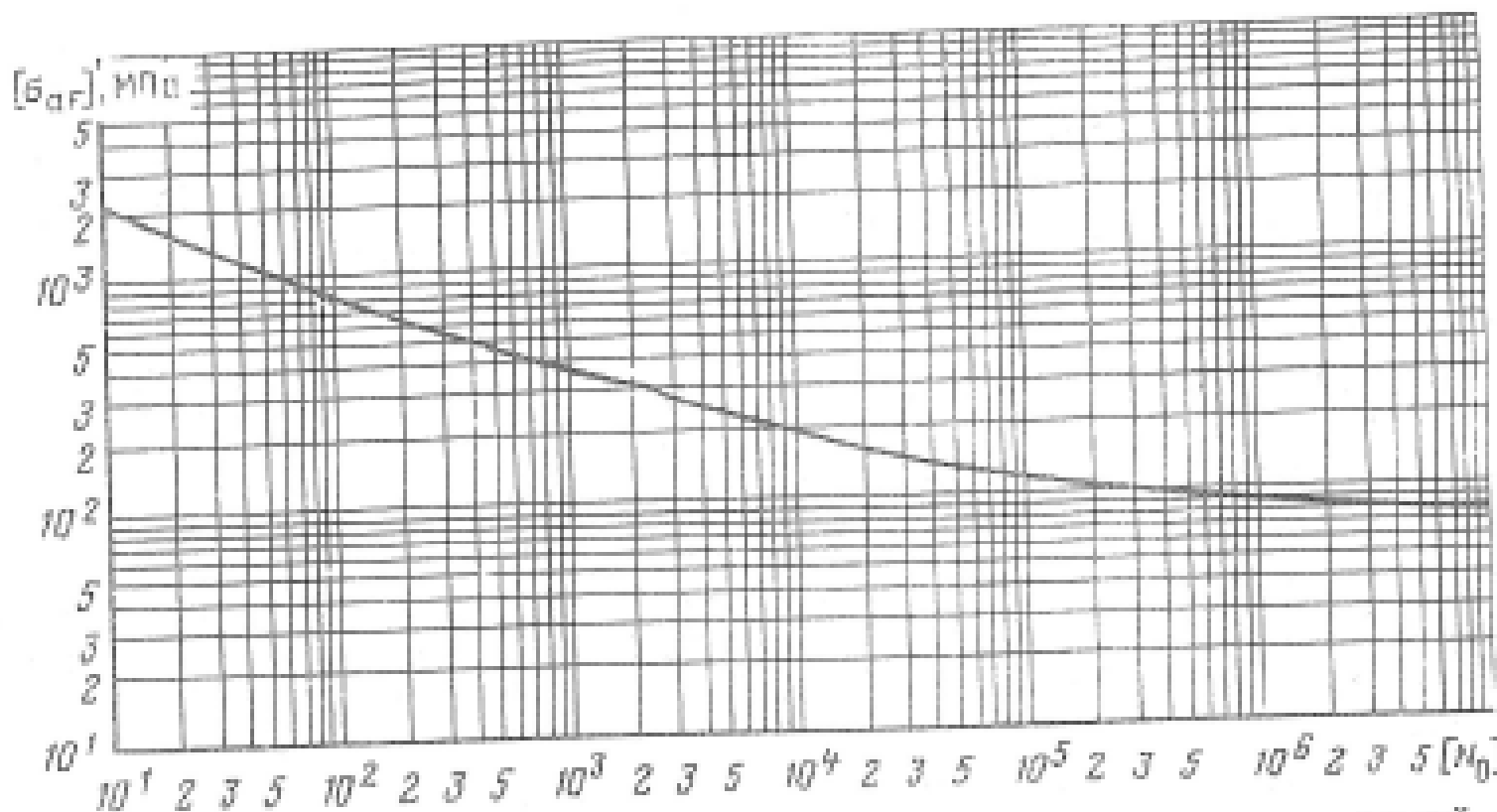


Рис. 5.5. Расчетная кривая усталости углеродистых и легированных сталей с  $R_{p0.2}^T/R_m^T \leq 0,7$  до  $T=623$  К ( $350^\circ$  С)



# CORROSION

- ❑ Corrosion is the reaction of a substance with its environment that causes a detectable change which can lead to deterioration in the function of the component or structure. In the present context, the material is steel and the reaction is usually an electrochemical reaction. The appearance of corrosion is governed by the so-called corrosion system consisting of the metal and the corrosive medium (the environment) with all the participating elements that can influence the electrochemical behavior and the corrosion parameters.

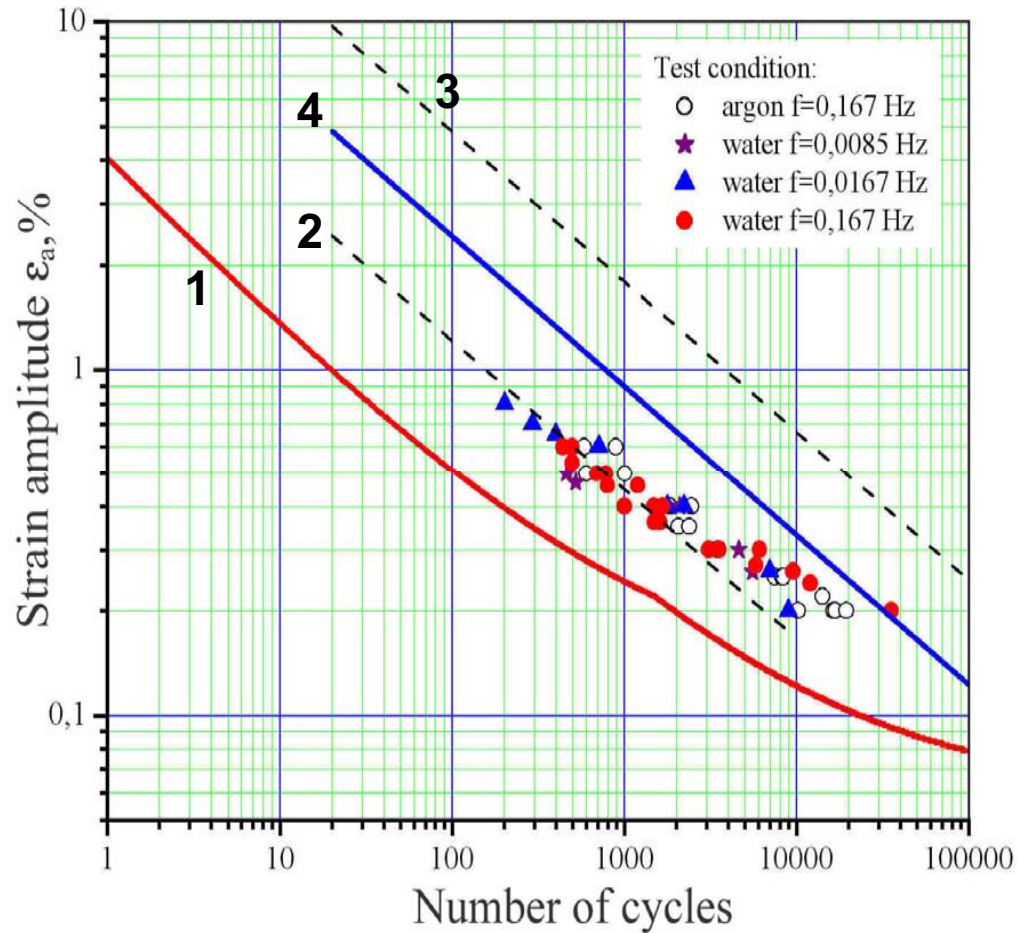


# CORROSION

- The variety of possible chemical and physical variables leads to a large number of types of corrosion, which can be subdivided into:
  - corrosion without mechanical loading (uniform corrosion and local corrosion attack, selective corrosion attack as e.g. intergranular corrosion)
  - corrosion with mechanical loading (stress corrosion cracking, corrosion fatigue) - and synergistic effects of neutron irradiation (irradiation assisted stress corrosion cracking);
  - flow assisted corrosion attack (erosion-corrosion, flow induced corrosion, cavitation).



# EFFECT OF ENVIRONMENT ON LOW CYCLE FATIGUE OF 15Cr2MoVA STEEL



- 1 – Reference curve for low alloyed steel in Russian Code PNAE G-7-002-86
- 2 and 3 – data falling outside the 5 and 95% tolerance bounds for steel at 20°C
- 4 – mean square dependence for the scatter band for steel at 20°C



# CORROSION

- ❑ Water chemistry control during operation, as well as during shutdown, is very important with respect to avoiding corrosion problems. Thus the content of all additives has to be carefully monitored and the ingress of impurities has to be strictly avoided e.g. during stand-still periods and maintenance work.





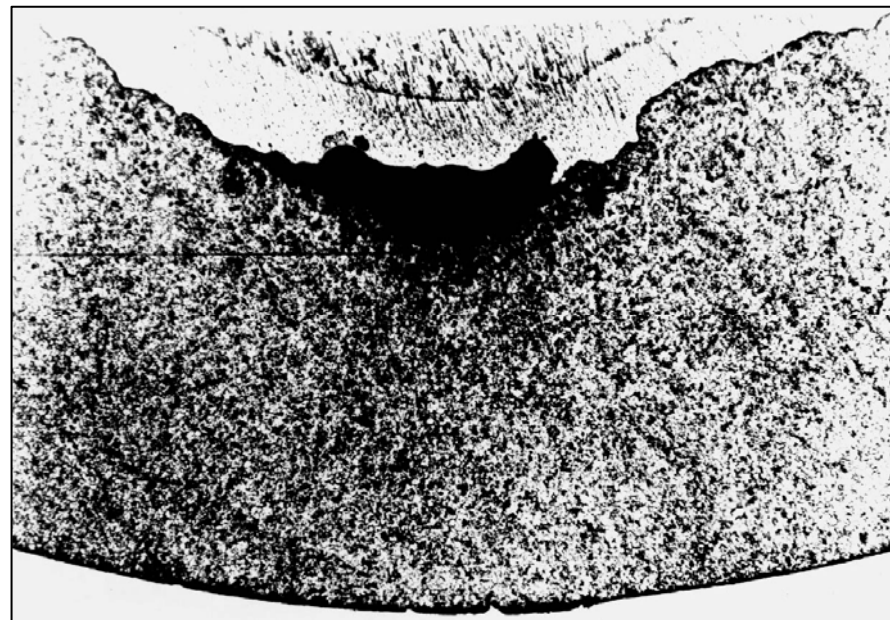
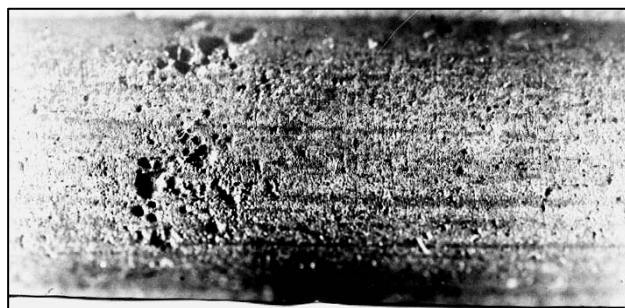
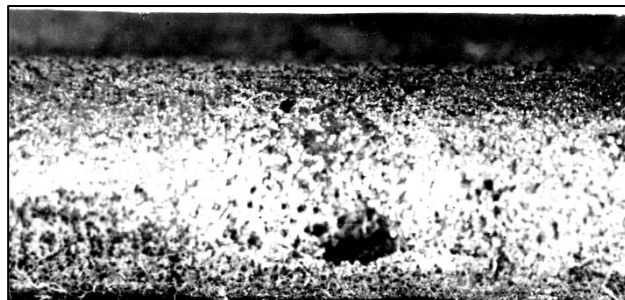
# CORROSION

- Primary Water Stress Corrosion Cracking (PWSCC)**
  - Intergranular stress corrosion cracking
  - Transgranular stress corrosion cracking
  - Irradiation assisted stress corrosion cracking
- General corrosion and pitting on the inside surfaces**
- Boric acid corrosion of outer surfaces**
- Erosion corrosion**





# TYPICAL CORROSION DAMAGES ON INNER SURFACE FOR UNCLADDED WWER-440



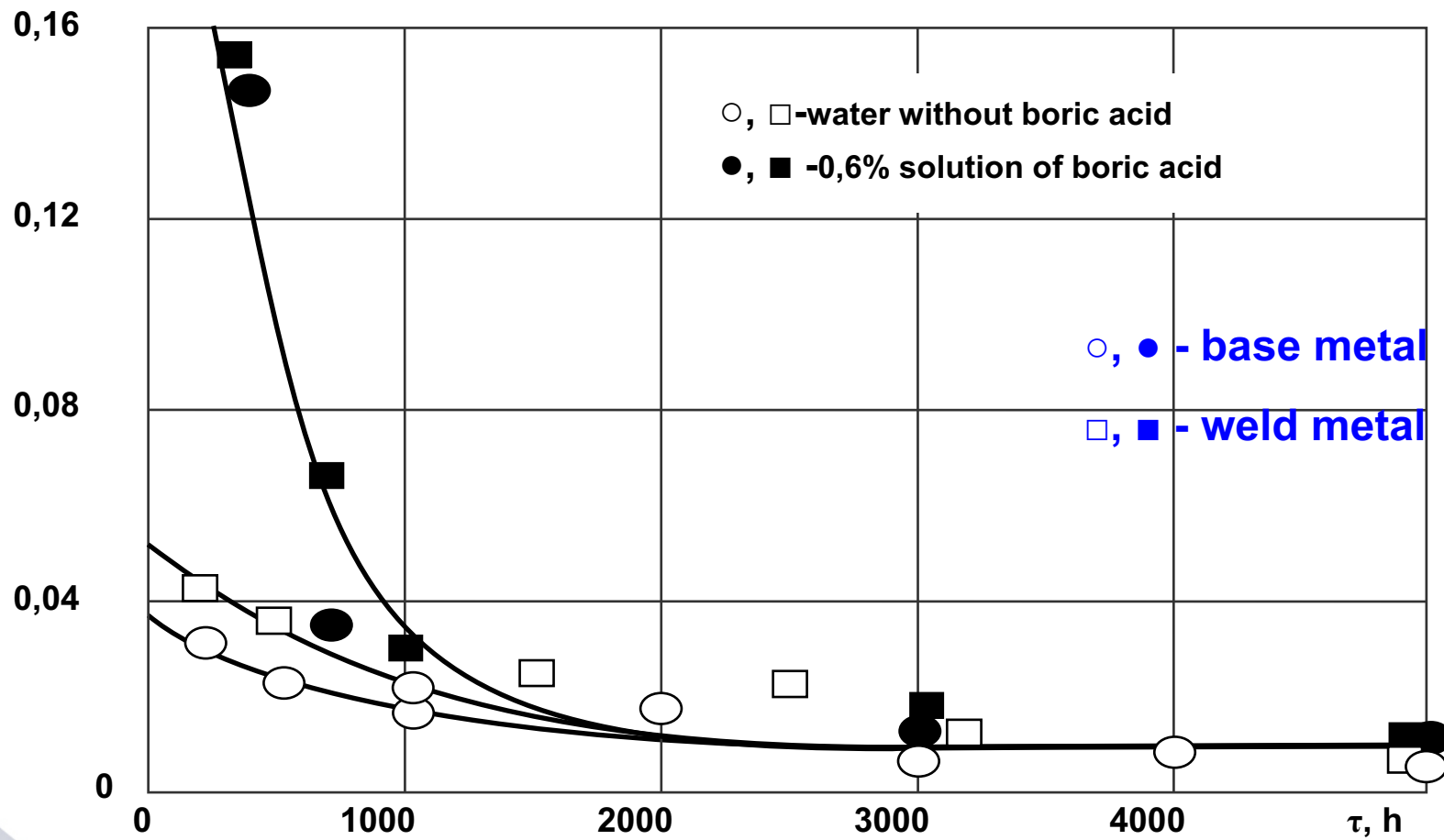
pits

pittings



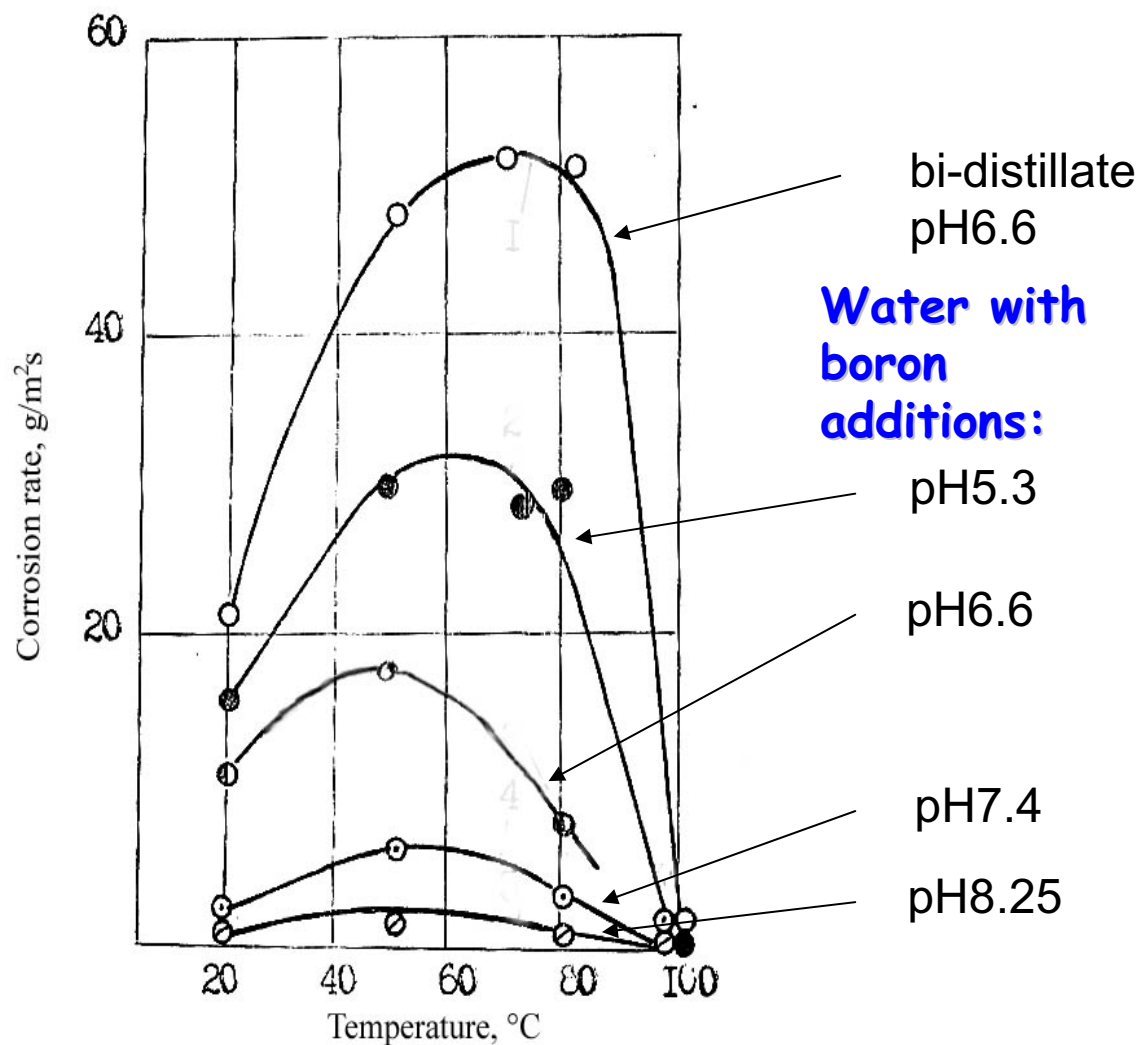
# EFFECT OF BORIC ACID ON GENERAL CORROSION RATE OF 15Cr2MoVA STEEL AND WELD METAL AT 300°C

Corrosion rate, g/m<sup>2</sup>·h



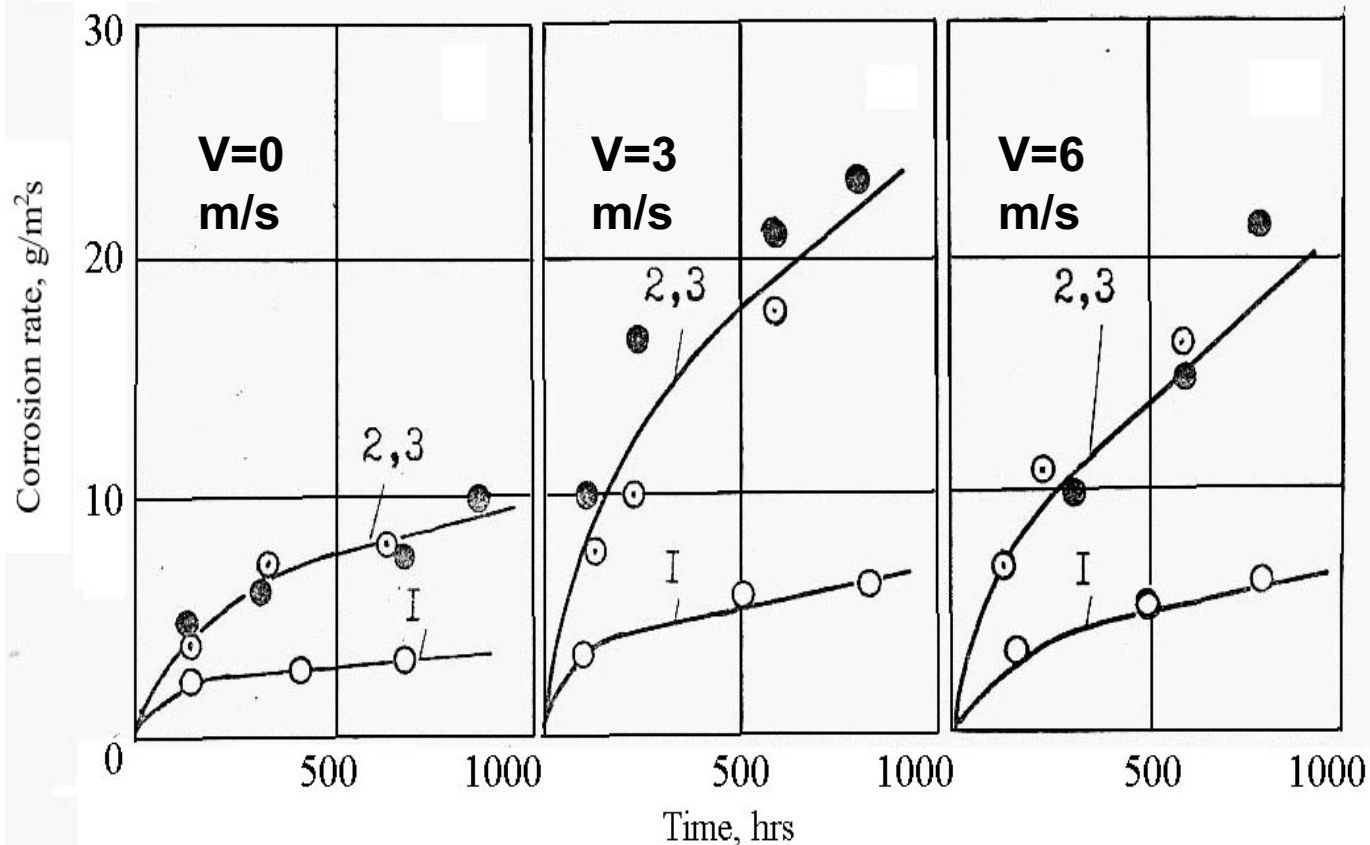


## CORROSION RATE OF 15Cr2NiMoV STEEL IN STOP-COLD REGIME





# EFFECT OF FLOW ENVIRONMENT ON CORROSION RATE OF 15Cr2NiMoV STEEL



**OPERATING CONDITIONS (p=12.5 MPa, T=290 °C, pH7)**

- 1- H<sub>3</sub>BO<sub>3</sub> - 5-6 g/kg, O<sub>2</sub> - 5-8 mg/kg, KOH -12-20 mg/kg
- 2- H<sub>3</sub>BO<sub>3</sub> - 5-6 g/kg, O<sub>2</sub> - 0,02 mg/kg, KOH -12-20 mg/kg
- 3- H<sub>3</sub>BO<sub>3</sub> - 5-6 g/kg, O<sub>2</sub> - 0,02 mg/kg, LiOH - 5-8 mg/kg

# CORROSION

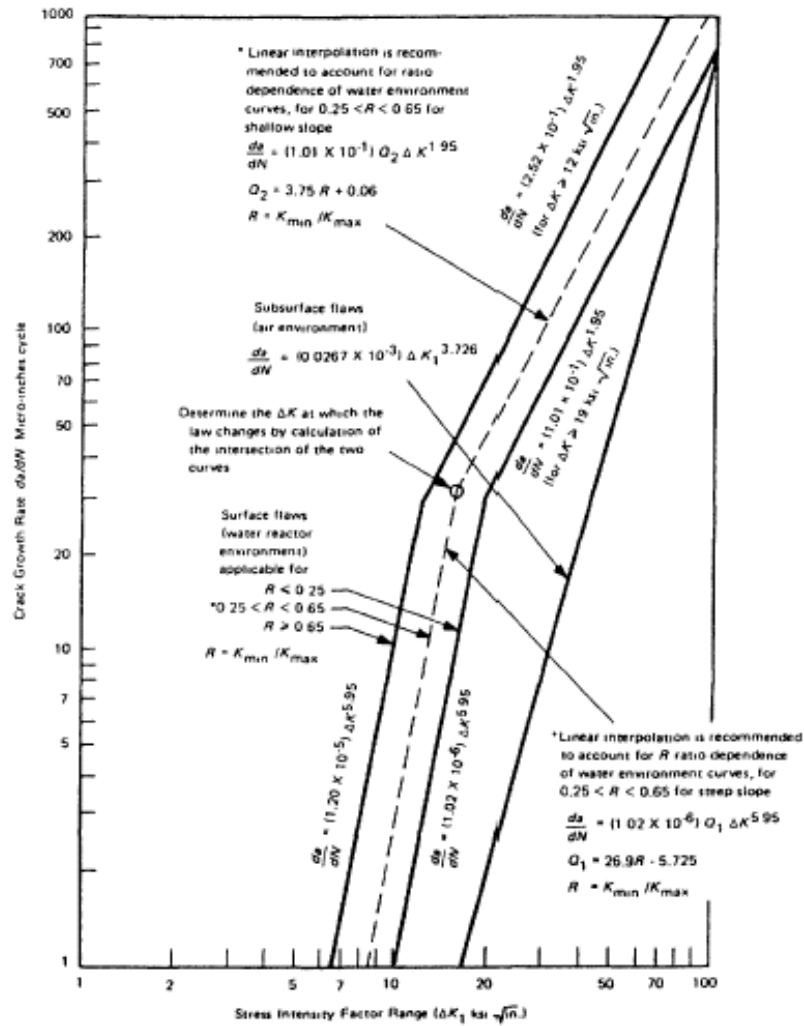
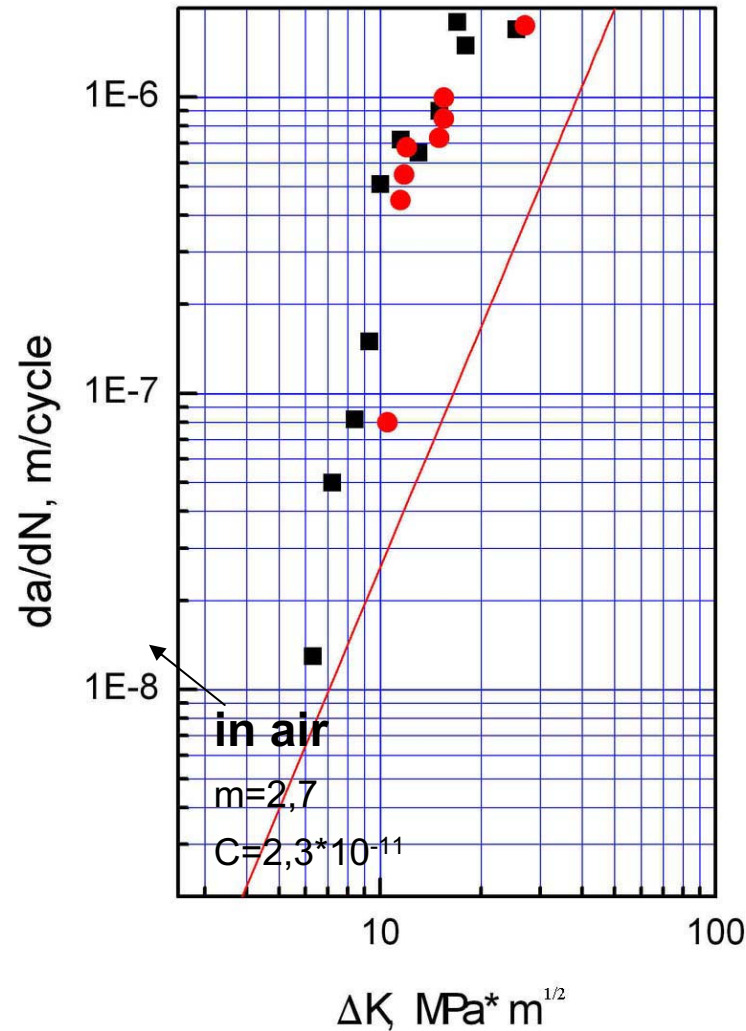


Fig. 6.2.12. Influence of corrosion on the cyclic crack growth rate in comparison to inert environment



# EFFECT OF ENVIRONMENT ON FCGR FOR 15Cr2NiMoV STEEL



Material:

15Cr2NiMoVA

15Cr2NiMoVAA

Test conditions:

T= 300 °C

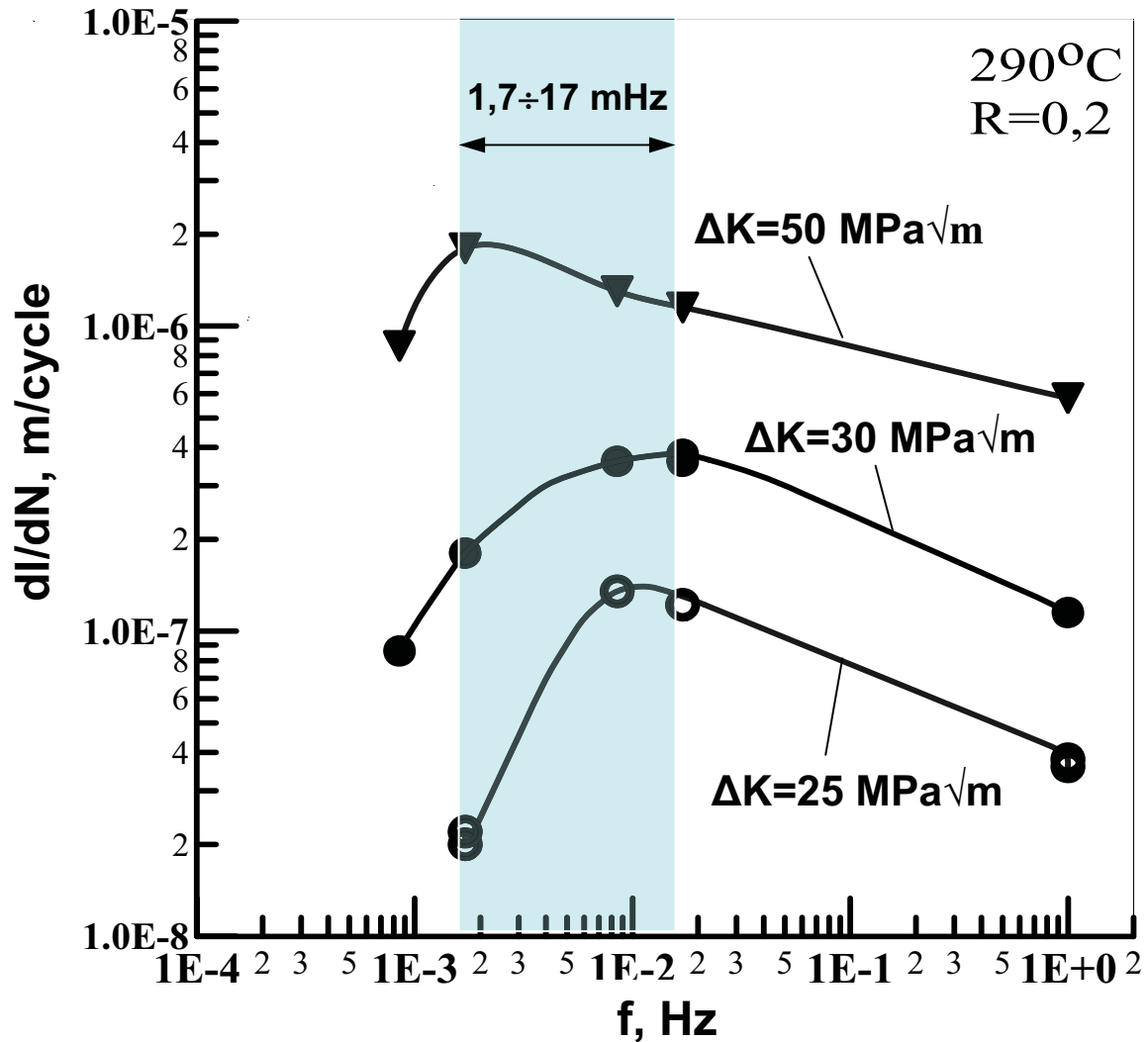
R= 0,7

Water PWR





# EFFECT OF FREQUENCY ON FCGR OF 15Cr2MoVA STEEL IN WWER ENVIRONMENT





# MECHANICAL WEAR

- This degradation type is broadly characterized as mechanically induced or aided degradation mechanism. Degradation from small amplitude, oscillatory motion, between continuously rubbing surfaces, is generally termed fretting. Vibration of relatively large amplitude, resulting in intermittent sliding contact between two parts, is termed sliding wear, or wear. Wear generally results from concurrent effects of vibration and corrosion



# MECHANICAL WEAR

- ❑ The major stressor in fretting and wear is flow induced vibration.
- ❑ Wear is defined as the removal of material surface layers due to relative motion between two surfaces or under the influence of hard



# MONITORING DEGRADATION

- Evidence on ageing and degradation are very important for optimising PLIM processes. Moreover, this evidence is often plant/component specific. Monitoring of degradation is very important in Plant Life Management and it encompasses direct detection and evaluation of degradation and also the monitoring of the parameters that can influence degradation mechanisms. It includes continuous (or on-line) monitoring, in service inspection, intermittent testing of specimens made from plant materials that can be installed inside components or in autoclaves.



# MONITORING DEGRADATION

																				Acoustic	
																				Vibration	
																				Stress wave emission	
																				Dimensional measurements	
																				X and gamma ray	
																				Ultrasonics	
																				Eddy currents	
																				Dye and Magnetic particle	
																				Visual	
																				TV	
																				Photography	
																				Leak detection	
																				Hardness	
																				Electrochemical	
																				Internal monitoring specimens	
																				External monitoring specimens	
<b>THERMAL</b>																					
Strain ageing				?	?																x x
475C embrittlement				?	?																x x x
Temper embrittlement																					x x
Sigma embrittlement				?	?																? x x
Age hardening/softening				?	?																x x x
Sensitisation																					x
<b>IRRADIATION</b>																					
Embrittlement																					x x
Helium embrittlement																					x
Irradiation growth						x															
<b>CORROSION</b>																					
Gen corr <sup>2</sup> /oxid <sup>2</sup>							x	x													x x
Galvanic									x	x		x	x	x							x x x
Crevice							x	x		x	x	x									
Erosion							x	x		x	x	x									
Pitting							x	x		x	x	x	x								
Cavitation							x	x		x	x	x									
Intergranular							x	x	x												
Gas Oxidation							x	x													x x
<b>HYDRIDING OF ZIRCONIUM</b>																					
<b>WEAR</b>																					
Sliding							x	x		x	x	x	x								
Fretting							x	x		x	x	x	x	x							
Impact							x	x		x	x	x	x	x							
Stiction/friction																					
<b>CRACKING</b>										x	x	x	x	x	x	x	x				
<b>DEFORMATIONS</b>							x	x	x												x x x



# MONITORING DEGRADATION

Goals		Methodology
Prevention from failures and damages	Load (height, frequency) Verification of specified load collective	On-line measurement of global plant data (p, T) Transient book-keeping Local temperature distributions Calculations related to the load collective
	Stresses (height, frequency) Verification of calculated design limits	On-line measurement of global plant data (p, T) Local measurement of temperatures, strains, displacements Calculation of fatigue usage
	Environment (oxygen content, pH, conductivity) Control of electrochemical potential Influence on protective oxide layers and fatigue strength	Measurement of plant data by sampling (sampling lines) Direct measurement at operating parameters, e. g. oxygen content (partially under development) Direct measurement of redox- and electrochemical potential





# MONITORING DEGRADATION

Early detection of damage	Loose parts monitoring  Loose parts, cracking, damage  Crack growth (during pressure test) Leakage monitoring system	On-line measurement and analysis of structure-borne acoustic signals (impact of loose parts), using e. g. piezoelectric accelerometers On-line measurement and analysis of vibrational behaviour (shifts in certain natural frequencies and amplitudes) using signals of the following categories: displacement (absolute, relative), pressure fluctuations, ex-core neutron flux noise On-line measurement and analysis of acoustic emission signals Visual inspection during operation Acoustic monitoring systems, using the noise generated by a leakage flow, detected by piezoelectric resonant acoustic emission probes Localisation of leaks Humidity measurement systems
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# MONITORING DEGRADATION

Measurement of crack depth and ligament	On-line measurement of crack growth by direct instrumentation of the affected component Potential probe Ultrasonic measurement
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# CONCLUSIONS

- ❑ ALL COMPONENTS ARE AFFECTED BY VARIOUS DEGRADATING MECHANISMS DURING THEIR LIFE
- ❑ SOME OF THESE MECHANISMS ARE IMPORTANT, SOME CAN BE NEGLECTED, SOME OF THEM CAN ARISE ONLY DURING LONG TERM OPERATION
- ❑ PROPER AND PLANNED MONITORING OF DEGRADATION MUST BE A PART OF ALL PLANT LIFE MANAGEMENT PROGRAMMES
- ❑ DETAILED ANALYSES OF ALL POTENTIAL DEGRADATING MECHANISMS IN INDIVIDUAL COMPONENTS ARE ALSO A PART OF „TLAA“ – TIME LIMITED AGEING ASSESSMENT FOR PLANT LIFE EXTENSION



# Thank you for your attention



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