

NUGENIA position on RPV Irradiation Embrittlement issues based on the outcome of the EURATOM FP7 project LONGLIFE

RPV Irradiation Embrittlement

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Foreword

The NUGENIA position paper on RPV irradiation embrittlement is a living document issued by NUGENIA Technical Area 4 "System and Component Integrity".

This NUGENIA position paper provides a state-of-the-art summary and describes open gaps of the specific technical field of RPV irradiation embrittlement that is in the scope of NUGENIA. The position paper is meant for an audience with a good knowledge on Gen II & III reactors, but without an in-depth knowledge of the specific technical field. Thus it provides a comprehensive state-of-the-art summary related to the regarded topic/position and comprehensive description of the open gaps of the dedicated technical field without being excessively detailed.

NUGENIA position papers clearly reference most recent projects on the dedicated technical field and are comprehensible without the referred documents. NUGENIA position papers are consensus documents, i.e. reflecting a common position of the "community" behind the document. The "community" does not only include the authors and contributors of the document, but in fact the whole technical area(s) from which the position paper in scope originates.



ABBREVIATIONS

APT	Atom Probe Tomography
CFR	Code of Federal Regulations (codification of the general and permanent rules and regulations of the federal government of the United States)
CRP	Copper-rich precipitate
DBTT	Ductile brittle transition temperature
EOL	End of Life
EEOL	Extended end of Life
ETC	Embrittlement Trend Curve
EURATOM	European Atomic Energy Community
FP7	Framework Programme 7 for Research and Technological Development of the European Union
IAEA	International Atomic Energy Agency
IAEA CRP	IAEA Coordinated Research Project
K _{Jc}	Static fracture toughness [MPa \checkmark m]; elastic-plastic (ASTM E1921)
LBE	Late blooming effect
LONGLIFE	Treatment of LONG Term Irradiation EmbrittLement Effects In RPV SaFEty Assessment (EURATOM FP7 project)
LTO	Long Term Operation
LWR	Light Water Reactor
MNP	Manganese-nickel-rich precipitate
MTR	Material Test Reactor
NPP	Nuclear Power Plant
NUGENIA	NUclear GENeration II & III Association, an international non-profitmaking association according to Belgian law, was established on 14th November, 2011 to become the unique framework for collaborative R&D in the scope of Generation II & III nuclear systems
NULIFE	Nuclear plant life prediction (European network of excellence in EURATOM FP6)
PAS	Positron annihilation spectroscopy
PERFORM60	Prediction of the Effects of Radiation FOR Pressure Vessel and in-core Materials using multi-scale Modelling – 60 years foreseen plant lifetime (EURATOM FP7 project)
RPV	Reactor Pressure Vessel
RT _{NDT}	Reference Nil-Ductility Transition Temperature [°C]
SANS	Small-Angle Neutron Scattering



 T_{41} Temperature [°C] at which a Av,T mean curve measured on transverse specimens
reaches 41 J T_0 Reference temperature [°C], the temperature on the Master-Curve at $K_{Jc} = 100 \text{ MPa} \checkmark m$ TEMTransmission electron microscopyWWERWater-Water Energetic Reactor Δ Shift



7 May 2015

INTRODUCTION

During service RPV steels are exposed to neutron irradiation, which causes microstructural changes and a degradation of the mechanical properties. As the ages of existing NPPs are increasing and lifetime extensions and EOL up to 80 years for existing and new NPPs are on the agenda, some existing open issues regarding the understanding and prediction of RPV irradiation embrittlement need to be addressed. Moreover, especially for materials with higher contents of Cu, P, or Ni, irradiation embrittlement effects resulting from long irradiation times and high neutron fluences must be adequately considered in RPV irradiation surveillance and safety assessment. Up to now, high fluence data for original RPV materials are largely used in national research programs but the RPV surveillance database for long irradiation times (>20 years) and low neutron flux is sparse. Consequently, the treatment of such long term irradiation effects is often afflicted with large uncertainties, requiring the generation of appropriate data and their assessment. In this context, the availability of microstructural data is essential for the development in understanding of the underlying mechanisms. Over the long term, further qualification and validation of appropriate safety concepts, such as Master Curve, are also important because the use of accurate tools together with reasonable incorporation of conservatisms are required for the assessment of long term operation. Finally, the application of well developed and validated prediction tools for irradiation embrittlement would be advantageous for the implementation of any dedicated safety assessment approach and for making decisions with respect to the remaining economic lifetime of nuclear power plant [1].

This position paper gives an overview on the State-of-the-Art of the RPV irradiation embrittlement issues based on the outcome of the EURATOM FP7 project LONGLIFE (Treatment of **LONG** Term Irradiation EmbrittLement Effects In RPV SaFEty Assessment) [1].

In this context the EURATOM FP7 project PERFORM60 (**P**rediction of the **E**ffects of **R**adiation **FOR** Pressure Vessel and in-core **M**aterials using multi-scale Modelling – **60** years foreseen plant lifetime) is worth mentioning. The objective of PERFORM60 was to develop future tools useful for industrial and research projects, related to the prediction of materials behavior under nuclear power plants operating conditions.



OVERVIEW ON CURRENT STATE OF KNOWLEDGE

Database

The essential mechanisms of RPV irradiation embrittlement, e.g. the dominant role of Cu-rich clusters for hardening/embrittlement in Cu-bearing RPV steels, are well known and confirmed by experimental data obtained from RPV surveillance programs in which representative steels are irradiated in capsules, retrieved and then tested. Those capsules are located on the inside of the RPV near the core where the neutron flux is ideally several times higher than in the RPV itself. In this way early estimates of RPV embrittlement can be provided in terms of material property data measured by tensile, Charpy-V and fracture toughness testing. Accelerated test-reactor irradiation programs have also been conducted to study irradiation embrittlement of RPV steels. Over decades, the test data have provided an increasingly large database for assessing and predicting irradiation embrittlement and for studying the underlying mechanisms. This notwithstanding, the data base for long irradiation times well beyond 40 operational years and high neutron fluences is sparse.

Embrittlement mechanisms

The most important embrittlement mechanisms are matrix damage (lattice point-defects and their clusters, such as dislocation loops and vacancy clusters which may grow to nanovoids), formation of Cu-rich precipitates (CRP, with Ni, Mn, Si, ...), formation of MnNi-rich precipitates (MNP, with Cu, Si, ...) and P segregation on grain boundaries. According to [2] the primary mechanism of embrittlement is the hardening produced by nanometer features that develop as a consequence of irradiation. The key embrittlement processes, illustrated in Figure 1, are:

- Generation of lattice defects in displacement cascades produced by high energy recoil atoms from neutron scattering and reactions. The primary defects are in the form of single and small clusters of vacancies and self-interstitials: these are assumed to be the primary constituents of the so-called matrix damage (Figure 1, a).
- Enhanced diffusion rates leading to the formation of nanoscale defect solute cluster complexes, solute clusters, and distinct phases, primarily copper-rich precipitates (CRPs) but also Mn-Ni-Si precipitates or clusters. The latter are sometimes assumed to appear in large volume fraction at high fluence (late blooming phases), potentially leading to sudden increase of hardening and embrittlement (late blooming effects) (Figure 1, b). The mechanism of formation of MNPs is not fully understood. Based on LONGLIFE experimental results, consistent with atomistic simulation results from PERFORM60, it was suggested that Mn, Ni and Si segregate to irradiation-induced loops to grow later to three-dimensional MNPs. But experimental evidence is poor (essentially based on the occasional observation by APT of Mn-Ni enriched clusters that look toroidal).
- Dislocation pinning and hardening by these nanofeatures (Figure 1, c).
- Hardening-induced increases in the fracture transition temperature (Figure 1, d and Figure 1, e).

The above embrittlement mechanisms become significant for neutron fluences exceeding $1 \cdot 10^{17}$ cm⁻² (E > 1 MeV) for which an irradiation surveillance program is required [2].





Figure 1: Basic embrittlement processes: (a) creation of primary radiation damage defects: (b) formation of nanoscale solute and defect clusters; (c) pinning of dislocations and hardening by nanofeatures; (d) hardening enhanced cleavage fracture; at a (e) stress concentration [2]

Irradiation induced change of mechanical properties

The above key embrittlement mechanisms are responsible for the increasing hardening and embrittlement with increasing neutron fluence, which results in higher DBTT (ductile brittle transition temperature, e.g. T_{41} from Charpy tests) as shown in Figure 2. The relative importance of the three different mechanisms depends significantly on the chemical composition of the steel.



Figure 2: Scheme of irradiation embrittlement mechanisms calculated by a semi-mechanistic analytical model [4]

In a typical LWR, the neutron flux ranges between approximately 10^9 and 10^{12} n \cdot cm⁻² \cdot s⁻¹. For Western LWRs, neutron energies greater than 1 MeV are used for correlations, while 0.5 MeV is used as the threshold for WWERs. RPV temperatures are usually in the range between ~260 to 300 °C. Regarding their effects on material properties, the ultrafine (nanometer) microstructural features (so-called nanofeatures) act as effective obstacles which require increased stress to move dislocations through or around them. As radiation exposure increases, the volume fraction of ultrafine scale obstacles increases and higher stresses are required for dislocation motion with a resulting increase in the yield strength of the



material. In this context the efficiency of different kinds of obstacles that contribute to the total hardening, the correct interaction model, and the rule of superposition are the issues of interest; all these issues can nowadays receive valuable support from physical models and computational physics modelling tools. The increase in yield strength means that higher temperatures are necessary to keep the yield strength below the cleavage fracture strength, especially near the tip of a crack where large stress and strain concentrations exist. Thus, the DBTT is increased, which is the measure used to describe the radiation-induced embrittlement (ΔT_{41} and ΔT_0 usually). For some steels, non-hardening embrittlement can be caused by radiation-induced solute segregation to grain boundaries. This type of embrittlement, frequently associated with segregation of phosphorous, can manifest itself as intergranular (grain boundary) fracture, rather than the usual transgranular cleavage fracture [5].

Concerning the development of predictive models, the synergistic effects of neutron fluence, flux and spectrum, irradiation temperature, chemical composition and the initial microstructure of the steel must be understood in order to minimize uncertainties. Some variables play a more important role than others, e.g. composition and temperature play a first order role to determine embrittlement versus fluence, and neutron spectrum and initial microstructure play, if any, a second order role, whereas neutron flux is a key variable to be understood due to its importance in order to transfer data from MTR and surveillance to LTO.

In addition to the basic strength and toughness properties, other properties are often determined, especially within research programs, to provide information relevant to developing a deeper understanding of material behavior [5].

The most common mechanical properties and their measured quantities are summarized in Table 1.

Property	Test rate	Measurement	Notch type	Test method examples			
Strength yield ultimate	Quasi-static	R _{p0.2} R _m	None	Tensile test; e.g. ASTM E 8, EN 10002-1, EN 10045-1			
Notch impact toughness energy Lateral expansion % shear fracture	Dynamic	$\begin{array}{l} T_{41 \!$	Blunt	Charpy V-notch (CVN) impact test; e.g. ASTM E 23, EN ISO 148. Obtain curve fit to data versus test temperature, determine various transition temperature indices, e.g. T_{4JJ} and USE. Initiation and propagation test			
Nil ductility transition temperature	Dynamic	T _{NDT}	Blunt changes to sharp	Drop-weight specimen test; e.g. ASTM E 208 Uses brittle weld crack starter on test specimen Propagation test			
Fracture toughness cleavage fracture Ductile fracture	Quasi-static Dynamic Quasi-static Dynamic	K _{Ic} , K _{Jc} , K _{Id} , K _{Jd} , J _{Ic} , J-R J _{Id}	Sharp crack produced by fatigue	Fracture toughness test of fatigue pre- cracked specimen; e.g. ASTM: E 399, E 1820, E 1921, ESIS P2-91D, ISO 12135, BS 7448, EN ISO 12737. J-R test is propagation test, others are initiation tests			
Crack-arrest toughness	Quasi-static load then dynamic propagation	K _{Ia}	Blunt changes to sharp	Crack-arrest test with notched specimen; e.g. ASTM E 1221 Propagation test			
Hardness		Η	None	Hardness test by indentation; micro-hardness by, e.g. ASTM E 92, EN ISO 6507-1			

Table 1: Mechanical properties of RPV steels [5]



In addition to those mechanical properties, there are common reference fracture toughness indices used for RPV steels given in Table 2. These indices are used in various ways to normalize fracture toughness of RPV steels. Changes in the physical properties of RPV steels are minimal [5].

	Table 2:	Reference	fracture	toughness	indices	[5]
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Index	Notation	Description
Nil ductility transition temperature (NDTT)	T _{NDT}	Drop-weight test by ASTM E-208 to determine temperature above which material toughness results in arrest of brittle propagating crack.
Reference temperature NDT	RT _{NDT}	Combination of drop-weight NDTT and CVN impact tests by ASME Code (see Sections 3 and 5 for additional details).
Reference fracture toughness temperature T_{θ}	T ₀	Quasi-static fracture toughness testing by ASTM E 1921 to measure cleavage initiation fracture toughness, K_{J_C} under elastic–plastic conditions of minimum no. of specimens. Master Curve is fitted to results to get T_0 at 100 MPa \sqrt{m} for results size adjusted to 1T specimen size.
Reference temperature RT_{T0}	$\mathrm{RT}_{\mathrm{T0}}$	Specified in ASME Code Cases N-629 and N-631 as $RT_{T0} = T_0 + 35^{\circ}$ F (19.4°C) and used in place of RT_{NDT} to index the ASME K_{Ic} curve.
Critical temperature of brittleness T_k	T_k	Specified in the Russian Code as a reference transition temperature based on the temperature at a specified Charpy impact energy; the energy level is specified based on the material yield strength, $R_{p0.2}$ (see Section 5 for additional details).

Impact of chemical composition

Copper has the greatest effect on irradiation sensitivity, but nickel and phosphorus are also strong contributors [5]:

- Copper is one of the elements that has the most deleterious effects on the irradiation-induced embrittlement of RPV steels. This effect appears from a copper content of about 0.04% (when the solution is supersaturated at RPV operating temperatures) and becomes very strong above 0.1%. From the 1970s, the total copper content in RPV steels and their welds has been limited to a maximum value of 0.1%, and to even lower values in most Western countries.
- Nickel effects have been extensively studied from the beginning of the 1980s. This element has a strong, and so far not fully explained, deleterious impact on irradiation-induced embrittlement of RPV steels. This impact may become very significant for nickel contents higher than about 1 or 1.2% and increases with the copper content in a synergetic way. [Remark: Ni does not require the presence of Cu to unfold its deleterious effect, at least if Mn is present.]
- Phosphorus has a well known deleterious effect on thermal ageing of ferritic steels due to its propensity to intergranular segregation. The phenomenon is known as thermal equilibrium segregation and is particularly significant in the temperature range 350 to 600°C. To limit or avoid this phenomenon, chemical compositions of ferritic steels have been optimized for many years (specification for P content, addition of Mo, etc.). In parallel, several models have been developed to forecast the phosphorus content in grain boundaries. In spite of this optimization, a deleterious effect of phosphorus on irradiation-induced embrittlement of RPV steels was revealed from the early 1970s. For concentrations higher than about 0.015%, experimental programmes showed that the shift in the Charpy transition curve was strongly reinforced as the phosphorus content increased. No significant effect on hardness or yield stress was reported, implying a temper embrittlement type of effect. Experimental results are insufficient to allow the dependence of P segregation on parameters such as dose rate or irradiation temperature to be determined. Since the beginning of the 1970s, the phosphorus concentration in RPV steels and their welds has been



limited to a maximum value of 0.015% and, later, even lower values, in most West European countries.

Manganese has not yet been the subject of many dedicated experimental studies. Consequently, its impact on irradiation-induced embrittlement is not so well characterised. Manganese contents in RPV steels were expected to be lower than the solubility limits of this element at temperatures of stress-relief heat treatment and irradiation (about 2.8 and 3%, respectively, in pure iron). However, as mentioned above, thermodynamics and experimental studies have shown that, in operation, manganese can integrate with copper-rich precipitates. It also participates in the Ni/Mn rich clusters that might or not be precursors for late blooming phases if any. In a recently completed IAEA CRP, it was noted that "For a given high level of nickel in the material and all other factors being equal, high manganese content leads to much greater irradiation induced embrittlement than low manganese content for both WWER-1000 and PWR materials".

Concerning the effect of Mn a thorough review was done in [6]. Moreover, experimental data (e.g. from SANS and APT) indicate that Mn appears first, prior to Ni to form MNPs.

With respect to the Cu-effect, which is already evident at relatively low fluences (and was therefore recognized early in history), it is worth to note that once the matrix Cu is consumed by CRPs, Cu no longer has a deleterious effect; then Ni becomes dominant. There are no data available to show whether the effect of Ni saturates at higher fluences. Moreover, the Cu effect can be reversed by thermal annealing to coarsen the precipitates, which has the effect of reducing the embrittlement rate on reirradiation.

Evidence also points to contributions of vanadium and silicon.

Most of the irradiation predictive formulas around the world variously include copper, nickel and phosphorus contents [5].

Flux effect

Many experiments have been carried out to assess flux effects on irradiation-induced embrittlement of RPV steels. The interpretation of available data is not straightforward due to a large variety of experimental conditions (ranges of flux, chemical composition, etc.). For NiMnMo steels containing standard levels of Ni and Mn, it was agreed that three different scenarios are of interest [5]:

- For steels containing a low level of copper (Cu less than about 0.1%), there is no significant flux effect in a range of flux below a threshold value (about 10¹² n · cm⁻² · s⁻¹, E > 1 MeV at 290°C) and irradiation temperatures between 150 and 300°C;
- For steels containing a significant amount of copper and irradiated to relatively low fluence (before the saturation of copper-related hardening), three regimes are expected according to the range of flux. One can expect a flux dependence at high (≥7 · 10¹⁰ n · cm⁻² · s⁻¹, E > 1 MeV at 290°C) and low (no consensus on the threshold) flux regions, and a regime of flux independence at intermediate fluxes;
- For steels containing a significant amount of copper and irradiated to relatively high fluence (after the saturation of copper-related hardening), results support the flux independence of the copper-related hardening in the saturation region. If the flux is not too high (lower than approximately 10¹² n · cm⁻² · s⁻¹, E > 1 MeV at 290°C), the total hardening should be dose independent.

For steels containing high levels of Mn and Ni (>1.2%), results are too sparse to draw conclusions. However, it is noteworthy that results yielded by Williams and co-workers show that the embrittlement of low copper steels (Cu < 0.1%) with 1.6% Ni and 1.2–1.7% Mn is flux independent [5].



SUMMARY OF THE LONGLIFE PROJECT

Scope of work

The 4-year project LONGLIFE (Treatment of long-term irradiation embrittlement effects in RPV safety assessment) was initiated under the EURATOM 7th Framework Programme of the European Commission in 2010 as an umbrella project of NULIFE [1], later integrated in NUGENIA, with the purpose of assessing the relevance of high neutron fluence and flux effects in RPV steels, in connection with the envisaged extension of NPP lifetimes from 40 up to 80 years.

The consortium consisted of 16 European research organizations and industrial companies. The project aimed at improved knowledge of LTO phenomena relevant for European LWRs, the assessment and proposed improvements of prediction tools, codes and standards, and the elaboration of best practice guidelines on RPV irradiation surveillance. The following specific issues were studied on preselected RPV materials and congeneric model alloys:

- <u>High fluence behavior</u> in terms of observations of any additional damage mechanisms, which have not been seen at fluences corresponding to the designed EOL of existing reactors (i.e. up to 40 years of operation). Understanding high fluence behavior is also related to judging the appropriateness of existing trend curves for prediction of irradiation-induced changes in material properties at fluences corresponding to an extended EOL of 80 years.
- <u>Neutron flux effect</u> as an important issue concerning the use of data obtained from accelerated material test reactors and surveillance irradiation data from power reactors to predict the hardening and embrittlement behavior of RPV materials in the core belt region.
- The so-called <u>late blooming effects (LBE)</u> which may occur at high fluences, preferably in low Cu steels which contain significant amounts of Ni and Mn. These late-in-life irradiation effects might have implications for RPV safety assessment under LTO conditions.
- The <u>effect of alloying and impurity elements</u>, such as Ni, Mn, Cu and Si, on the irradiation-induced changes in material properties.
- <u>Thermal ageing</u> of RPV steels as a general degradation mechanism connected with long term operation at high temperature, which may have some synergism with radiation effects for some steels.
- The issue of <u>P-segregation</u> and non-hardening embrittlement may be important for RPV steels with higher P-content, but the actual relevance is not yet clear.

The experimental investigations in terms of material testing and microstructural analyses were based on 16 pre-selected materials classed into various RPV material groups with both base and weld materials chosen for their significant sensitivity to specific long term irradiation effects, including one RPV steel from a decommissioned plant (EDF-1), see Table 3 and Table 4.

Most of the pre-selected materials are representative of Western LWRs and WWER reactors in operation [7].



ANP-2 P60	WM S3NiMo1	MTR	AP, SANS, TEM FT	
ANP-6 / RAB1	WM S3NiMo	MTR	AP, SANS, TEM, PAS	
ANP-5	WM 22NiMoCr3-7	MTR (evidence for flux effect)	SANS, PAS	
ANP-4 <u>P60</u>	BM 22NiMoCr3-7	MTR	SANS, TEM	Representative
SCK-6	BM 22NiMoCr3-7	MTR	TEM, PAS Tensile	Western LWR
EDF-1	BM 16MND5	Surveillance	AP, TEM	
EDF-2 <u>P60</u>	BM 16MND5	Surveillance	AP, SANS, TEM	
EDF-3 <u>P60</u>	WM 16MND5	Surveillance	AP, SANS, TEM	
FZD-1a	BM A533B high P (JPB)	MTR (evidence for LBE at Tirr=255°C)	AP, SANS, TEM, AES Tensile	Western LWR
FZD-1b	BM A533B low P (JPC)	MTR (evidence for LBE at Tirr=255°C)	AP, SANS, TEM, AES Tensile	Effects
FZD-2	WM 10KhMFT	Decomm. (Greifswald 4)	SANS, AES FT, SPT, Tensile, HV	VV/EB 440/220
VTT-1	WM 10KhMFT	Surveillance	SANS, TEM FT	VVER-440/230
AEK-1	BM 15Kh2MFA	MTR Decomm. (Greifswald 8, unirr)	AP, SANS, TEM FT, HV	VVER-440/213
NRI-6	BM+WM 15Kh2MFA	Surveillance	ТЕМ	
NRI-1	WM 5Kh2NMFAA	MTR	AP, TEM Impact, Tensile, HV	VVER-1000

Table 3: LONGLIFE materials and experimental matrix [8]

The overall objectives of LONGLIFE for supporting long-term RPV operation were:

- Improved knowledge on LTO specific irradiation phenomena relevant for European reactors
- Assessment of prediction tools, codes and standards
- Elaboration of best practice guide lines on RPV irradiation surveillance

The technical work comprised the analysis of LTO boundary conditions, microstructural investigations and supplementary mechanical tests on RPV steels, training activities, and elaboration of recommendations for RPV materials assessment and embrittlement surveillance under LTO conditions. A key part was the selection of relevant materials for examination, e.g. which contain different weld and base metals originating from European LWRs and allowed the issues described above to be examined. The scope of work covered different features of Western LWR and WWER type RPV materials [1].



Cada	Motorial	Chemical Composition [wt.%]									
Code	wateriai	С	Si	Mn	Р	s	Cr	Мо	Ni	Cu	v
ANP-2	WM S3NiMo1	0.05	0.12	1.08	0.019	0.009	< 0.10	0.62	1.01	0.03	0.01
ANP-6	WM S3NiMo	0.05	0.15	1.41	0.012	0.007	0.07	0.46	1.69	0.08	0.004
RAB-1	WM S3NiMo	0.052	0.21	1.46	0.009	0.006	0.07	0.5	1.58	0.08	0.002
ANP-5	WM NiCrMo1	0.08	0.15	1.14	0.015	0.013	0.74	0.6	1.11	0.22	0.01
ANP-4	BM 22NiMoCr3-7	0.21	0.22	0.85	0.006	0.006	0.39	0.55	0.84	0.05	<0.010
SCK-6	BM 22NiMoCr3-7	0.21	0.24	0.82	0.003	0.004	0.003	0.56	0.79	0.05	<0.010
EDF-1	BM 16MND5	0.169	0.31	1.27	0.01	0.005	0.15	0.39	0.65	0.09	0.02
EDF-2	BM 16MND5	0.138	0.22	1.32	0.006	0.006	0.2	0.54	0.69	0.064	<0.005
EDF-3	WM 16MND5	0.054	0.35	1.41	0.009	0.011	0.02	0.57	0.64	0.033	0.004
FZD-1a	BM A533B	0.2	0.24	1.3	0.020	0.004	0.17	0.57	0.74	0.027	0.005
FZD-1b	BM A533B	0.19	0.24	1.32	0.005	0.005	0.16	0.55	0.73	0.029	0.006
FZD-2	WM 10KhMFT	0.04	0.44	1.13	0.043	0.007	1.39	0.45	0.14	0.11	0.17
VTT-1	WM 10KhMFT	0.04	0.6	1.06	0.02	0.026	1.57	0.46	0.13	0.2	0.2
AEK-1	BM 15Kh2MFA	0.16	0.29	0.54	0.018	0.013	2.65	0.68	0.07	0.09	0.28
NRI-6	WM 15Kh2MFA	0.031	0.6	1.13	0.01	0.015	1.31	0.52	0.05	0.06	0.19
NRI-1	WM 5Kh2NMFAA	0.07	0.37	0.74	0.006	0.008	1.86	0.68	1.67	0.04	-

Table 4: LONGLIFE materials and chemical composition

Discussion of results

Flux effect

A significant flux effect on microstructure was observed for high copper weld materials, however not in material properties (Figure 3).

The following results were obtained from microstructural analyses of RPV steels irradiated up to the same fluence at different fluxes (ANP-5, VTT-1 and two additional materials):

- PAS indicates greater increase in vacancy concentration for the higher flux
- SANS indicates:
 - The size distribution of irradiation-induced clusters for the lower flux has a higher average radius and wider range, whichever the Cu content of the RPV steel
 - A slightly higher volume fraction of clusters for the lower flux, whichever the Cu content of the RPV steel
 - The larger sizes and slightly higher volume fraction are consistent with the observed lower number density of clusters at the lower flux
- TEM indicates more visible loops for the lower flux but no flux effect on loop size (Figure 4).



wt%	С	Si	Р	V	Cr	Mn	Ni	Cu	Мо
ANP-5 (WM)	0.08	0.15	0.015	0.001	0.74	1.10	1.11	0.22	0.60
VTT-1 (WM)	0.04	0.6	0.02	0.2	1.57	1.06	0.13	0.2	0.46



Bergner et al. J. Phys. Cond. Matt. 20 (2008) Reported flux effect confirmed in a 2nd SANS exp. Flux ratio ≈ 35 No effect on T_{CVN} nor R_{p02}



Flux effect on size distribution, but less pronounced than in ANP-5 Flux ratio ≈ 6

Figure 3: Flux effect on microstructure of high Cu weld materials [9]



low flux (0.28.1012 n/cm2s)

high flux (1.6.1012 n/cm2s)

Fluence, Φ (10 ¹⁹ cm ⁻²) (E>1MeV)	Flux, φ (10 ¹² cm ⁻² s ⁻¹) (E>1MeV)	Number density, <i>N</i> * (10 ¹⁶ cm ⁻³)	Mean diameter, <i>d</i> (nm)	Number of loops
4.0	1.6	0.062	3.81 ± 0.06	112
4.2	0.28	0.29	3.34 ± 0.2	178





High fluence behavior

With respect to the irradiation behavior at high fluences, the following common trends have been observed in terms of microstructure (Figure 5):

- Irradiation damage comprises of a relatively low number density of heterogeneously distributed dislocation loops, a high number density of Mn, Ni, Si, Cu, P rich clusters and segregation of the same solutes along dislocation lines and dislocation loops. Voids are detected at high fluence.
- The chemical composition of the solute clusters seems to be independent of the fluence.
- There is an increase of cluster size (very slow growth) and number density with increasing dose, resulting in an increase of their volume fraction.
- No observation of saturation of the clustering process at high fluence.

P Si Mn Ni Cu Fe



Solute atoms EDF 2 irradiated at 6.95×10¹⁹n.cm⁻². [*B. Radiguet LONGLIFE D3.3*]



Dislocation loops. TEM images EDF 2 irradiated at 6.95×1019n.cm-2. [E. Meslin LONGLIFE D3.9]



Voids. TEM images AEK-1 irradiated at 90.9x1019 n/cm2 (E>1MeV) at 275°C [M Hernandez-Mayoral LONGLIFE D3.9]

Figure 5: Different features observed by microstructural examinations [9]

The mechanical test data (T_{41}) of the LONGLIFE materials confirms that no saturation of the irradiation embrittlement was observed at high fluence (Figure 6).







Figure 6: T₄₁ data measured for LONGLIFE materials

Late irradiation effects

There are controversial viewpoints on the existence or not of "Late Blooming Effects" and whether they are really "Blooming" or not. For low-Cu steels it is not clear if the reason for LBE is the formation of clusters accelerating at high fluence or a delayed formation (incubation time). Moreover, none of the average chemical compositions detected match well with the LBP candidate G-phase composition [9]. However, a visible LBE in terms of unexpectedly higher irradiation embrittlement at higher fluences was measured for the LONGLIFE material ANP-2 (low Cu, medium Ni/Mn content) in both microstructure (Figure 7) and mechanical properties (Figure 8).





Figure 7: Volume fraction (by APT and SANS left) and cluster measurements (by APT, right) for LONGLIFE material ANP-2 [11], [12]



Figure 8: T_0 and T_{41} data measured by Charpy-V and Master Curve testing respectively for LONGLIFE material ANP-2 [11]

Four possible explanations for this unexpected material behavior of ANP-2 are given in [11]:

- Late Blooming Phases (may occur at high fluences, high Ni/Mn, low Cu, low T)
- Late irradiation effect (late acceleration but no new features)
- Scattering of data (inherent scatter of the Charpy and FT toughness test results)
- Impact of different take out locations of specimens used ("material variability")

However, the database is currently insufficient to allow clear reasons to be deduced for the effects observed for ANP-2 at higher fluences. With respect to LTO it is worth mentioning that a similar pattern of behavior has been observed in surveillance measurements, as shown in Figure 9.





Figure 9: Measured RT_{NDT} shifts from RPV irradiation surveillance data reported in [13]

Microstructural data of the material irradiated at the two highest fluences in Figure 9 have revealed that the chemical composition as well as number density of clusters does not change very much, while the cluster diameter increases with fluence, resulting in the increase in volume fraction of clusters [14]. The microstructural data supports the assumption that the late irradiation effect may be caused by accelerated (or continuous) growth of existing features rather than by formation of new features.

Macroscopic heterogeneity

An effect of macroscopic heterogeneity was observed in fracture mechanics testing of FZD-2 weld. In this case material inhomogeneities in the multi-layer weld are dominant over irradiation effects (Figure 10).



Figure 10: Fracture mechanics testing of FZD-2 material [9]

Thermal aging

Concerning thermal aging appropriate data representative of 60–80 years of operation (range of 500,000 h) are still missing and no additional thermally aged RPV steels were available for the investigation in the LONGLIFE project. No detrimental thermal ageing was observed in WWER-440 base material. In that case, exposure at 270 °C for 140,000 h actually produced a beneficial effect on the upper shelf energy [9].



Correlation of microstructure with mechanical properties

A correlation of microstructure (volume fraction v_f of solute clusters) with mechanical properties was found in the form of $\Delta T_{41J} \sim A^* \sqrt{v_f}$. Most of the measured data follow the expected linear relationship as shown in Figure 11. Some materials show different behavior, e.g. the material AEK-1, which was exposed to very high fluence [15], is clearly out of the general trend. The reasons of this deviation were revealed as a result of the LONGLIFE project. It was demonstrated by application of the three-feature dispersed-barrier hardening model [16], [17] that

- Cu-rich clusters are weak obstacles to dislocation glide but contribute most to hardening because of their high number density.
- Loops are stronger than Cu-rich clusters but weaker than nanovoids.
- Nanovoids are the strongest obstacles but they only contribute after accumulation of a high fluence beyond the range relevant for operating NPPs.

The deviation of AEK-1 is caused by matrix damage in form of heterogeneously-distributed dislocation loops and voids which are the origin of the extra-hardening observed at very high fluence [15], however nanovoids (and loops) are not considered in Fig. 11, but exist in AEK-1 (loops detected also in VTT-1 and NRI-1).

It can be concluded that the proportionality with $\sqrt{v_f}$ is applicable for operation relevant irradiation conditions.



Figure 11: Correlation of microstructure with mechanical properties measured for LONGLIFE materials [9]

Insights in microstructure

Further findings from the microstructural examinations in LONGLIFE are [18]:

- Higher Cu, Ni, Mn and possibly Si contents will increase the number density and volume fraction of solutes clusters induced during neutron irradiation
- Cu content (ANP-2 <EDF-3 <EDF-2 <ANP-6 <VTT-1) promotes solute clustering in the initial state of irradiation
- In low/medium Ni materials (EDF-2 and EDF-3 > ANP-2)
 - Mn promotes solute clustering
 - o Si has almost no effect



- Mainly NiMnSi-rich clusters are detected by SANS and APT results
- CRPs in Cu-rich materials (ANP-5, VTT-1)
- Materials with low alloying elements and impurities
 - o Change in material properties mainly caused by matrix defects
 - Low number of precipitates/clusters (e.g. ANP-4, AEK-1)
- Volume fraction and shift in T₄₁ are correlated (approx.: △T₄₁ ~ A*√v_f, where deviations from the correlation can be explained in terms of loops and nanovoids)
 - \circ Increase in volume fraction leads to increase in T₄₁

The high Ni (and Mn) content of weld material ANP-6 is responsible for the higher number density and volume fraction measured for this material where NiMnSi-rich clusters were found. More irradiation induced clusters with significant higher Ni and higher Mn, Si and Cu concentration were measured for ANP-6 compared to materials with lower Ni contents (see Figure 12).



Figure 12: NiMnSi-rich clusters measure by APT for a low (left) and high (right) nickel weld [18]

Embrittlement Trend Curves (ETC)

Another point of interest is the application of Embrittlement Trend Curves (ETC). None of the existing ETCs predicts the temperature shift sufficiently for all materials and there is a clear tendency that ETCs underpredict the irradiation embrittlement at higher fluences as can be seen in Figure 13. Beside the large scatter of the data there are limitations of the ETC models, e.g. all relevant chemical elements and the effect of microstructure are not explicitly considered [9]. Whilst, for example, existing trend curves such as 10 CFR 50.61a and Reg.-Guide 1.99 Rev. 2 represent well their databases, these do not extrapolate accurately the irradiation behavior at high fluence and for low Cu materials [19].





Figure 13: Application of ETCs to all LONGLIFE materials (left, [9]) and 10 CFR 50.61a predictions for RPV steels (right, [19])

Monitoring irradiation embrittlement during LTO

Finally, guidelines for monitoring irradiation embrittlement during LTO have been developed in LONGLIFE ([9], [11], [20]) including following issues (a few examples see Figure 14):

- Reconstitution and further irradiation
- Miniature specimens
- Use of surrogate material
- Additional capsules with higher lead factors
- RPV dosimetry and temperature monitoring
- Withdrawal schedules
- Integrated surveillance programs
- Mitigation measures (if required and based on monitoring results)



Figure 14: Examples for monitoring irradiation embrittlement during LTO [11]



OPEN ISSUES

The main research needs arising from LONGLIFE [9] are:

- Flux effect
 - Clarification of the role of unstable matrix damage (PIA of materials irradiated at different fluxes)
 - o Microstructural data for low Cu steels irradiated at different fluxes are needed
 - Correlation of microstructural data and mechanical properties supported by multi-scale modeling
- Conditions of presence or absence of late blooming effects
 - Critical analysis of cases of unexpectedly high hardening or embrittlement with respect to the general trend
 - o Specification of conditions favourable for the occurrence of LBE
- Critical assessment of existing embrittlement trend curves (ETC)
 - o Application of the latest ETCs, identification and analysis of outliers
 - Correlations between predicted DBTT and microstructural parameters (volume fraction, size and number density of defects etc.)

Concerning the late blooming effects there is also a need to identify the mechanisms potentially responsible for those effects (if any) based on physical modelling.

The so-called extended beltline issue should also be addressed for LTO because at longer operation times higher fluences are expected not only for the core beltline but also for an extended area where the fluence might exceed $1 \cdot 10^{17}$ cm⁻² (E > 1 MeV). Moreover, by means of scattering and reflections of neutrons (Albedo effect) the supporting structure and outer nozzle surface of the RPV might also be concerned during LTO.

Finally, the issue about the impact of the as delivered microstructure and of metallurgical macroscopic heterogeneities at initial state on the irradiation embrittlement should be addressed as well.

CONCLUSIONS

The overall conclusions of the LONGLIFE project can be summarized as follows [9]:

- Indications of late blooming effects seem to exist in some cases, however clear criteria for occurrence/exclusion in terms of irradiation conditions and chemical composition could not be defined.
- Flux effects were observed on microstructure in some cases (high-Cu materials). However these were not accompanied by significant effects on mechanical properties, and the underlying reasons for this are not clear.
- An effect of Phosphorus on hardening was observed.
- Experimental embrittlement and hardening curves do not show saturation at high fluences.



- In real welds, irradiation effects on mechanical behavior can be swamped by the influence of inhomogeneous mesoscopic structural effects.
- Master curve shape validity for high fluences:
 - the shapes of the Master Curve and Unified Curve are significantly different for materials with high T_0 levels, the Unified Curve being more conservative at high temperatures,
 - o large specimens would be needed, which are rarely available,
 - o the shape validity issue is not relevant for most RPV applications.
- None of the existing trend curve models predicts accurately the entirety of LONGLIFE database (FIM, RG 1.99, E900-02, EONY, JAEC, PNAE-G7).
- Surveillance guidelines for LTO have been developed:
 - o re-use of tested specimens,
 - o proposals for withdrawal between EOL and EEOL.

The conclusions given above are based on the final workshop presentations and are consistent with the final LONGLIFE report [21]. Moreover, the IAEA report [5] gives a good overview on most aspects of RPV irradiation embrittlement under LTO conditions.

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REFERENCES

- [1] J. May, H. Hein, E. Altstadt, F. Bergner, H. W. Viehrig, A. Ulbricht, R. Chaouadi, B. Radiguet, S. Cammelli, H. Huang, K. Wilford, FP7 project LONGLIFE: Treatment of long-term irradiation embrittlement effects in RPV safety assessment, 3rd International Conference on Nuclear Power Plant Life Management (PLiM) for Long Term Operations, Salt Lake City, May 13-17, 2012
- [2] Odette, G., Lucas, G.; Embrittlement of Nuclear Reactor Pressure Vessels, JOM 53 (7) pp. 18-22, 2001
- [3] ASTM E185, Standard Practice for Design of Surveillance Programs for Light-Water Moderated Nuclear Power Reactor Vessels, Designation: E185-10
- [4] Debarberis et. al., Semi-mechanistic analytical model for radiation embrittlement and reembrittlement data analysis, International Journal of Pressure Vessels and Piping, Volume 82, 2005



- [5] Integrity of Reactor Pressure Vessels in Nuclear Power Plants: Assessment of Irradiation Embrittlement Effects in Reactor Pressure Vessel Steels, IAEA Nuclear Energy Series No. NP-T-3.11, Vienna, 2009
- [6] R.B. Jones, "Influence of manganese on mechanical properties, irradiation susceptibility and microstructure of ferritic steels, alloys and welds", International Materials Reviews 56 (2011) 167-206
- [7] H. Hein, E. Keim, J. May, H. Schnabel, Some recent research results and their implications for RPV irradiation surveillance under long term operation, IAEA Technical Meeting on Degradation of primary components of Pressurised Water Cooled Nuclear Power Plants: current issues and future challenges, 5-8 November 2013, Vienna, Austria
- [8] E. Altstadt, Welcome and overview of LONGLIFE, LONGLIFE Final International Workshop, 15-16 January 2014, Dresden, Germany
- [9] E. Altstadt, M. Serrano, F. Gillemot, M. Brumovsky, H. Hein, I. O'Donnell, I. Marcelles, Conclusions from LONGLIFE, LONGLIFE Final International Workshop, 15-16 January 2014, Dresden, Germany
- [10] F. Bergner, M. Hernández-Mayoral, M. Serrano, V. Slugen, S. Ortner, K. Wilford, J. Barthelmes, H. Hein, J. Lim, A. Ulbricht, A. Wagner, Flux effect on the microstructure of neutron-irradiated RPV steels, LONGLIFE Final International Workshop, 15-16 January 2014, Dresden, Germany
- [11] H. Hein, Practical issues of RPV irradiation surveillance for LTO, LONGLIFE Final International Workshop, 15-16 January 2014, Dresden, Germany
- [12] E. Altstadt, E. Keim, H. Hein, M. Serrano, F. Bergner, H.-W. Viehrig, A. Ballesteros, R. Chaouadi, K. Wilford, FP7 Project LONGLIFE: Overview of results and implications, Nuclear Engineering and Design 278 (2014) 753–757
- [13] N. Soneda et al, High Fluence Surveillance Data and Recalibration of RPV Embrittlement Correlation Method in Japan, PVP2013-98076, Proceedings of the ASME 2013 Pressure Vessels and Piping Conference PVP2013 July 14-18, 2013, Paris, France
- [14] N. Soneda et al, Embrittlement of RPV steels due to formation of irradiation-induced solute atom clusters, IAEA Technical Meeting 5-8 November 2013, Vienna
- [15] M. Serrano, F. Bergner, B. Radiguet, J. H. Lim, C. R. M. Grovenor, M. Hernandez-Mayoral, E. Meslin, K. Wilford, W. Van Renterghem, J. Kocik, S. Ortner, H. W. Viehrig, R. Chaouadi, M. Brumovsky, H. Hein, F. Gillemot, P. Todeschini, T. Planman, J Rouden and E. Altstadt, Correlation between microstructural features and mechanical properties of irradiated LONGLIFE RPV steels, Fontevraud 8 - Contribution of Materials Investigations and Operating Experience to LWRs Safety, Performance and Reliability, France, Avignon, September 15-18, 2014
- [16] Bergner, F. Gillemot, M. Hernández-Mayoral, M. Serrano, G. Török, A. Ulbricht, E. Altstadt, Contributions of Cu-rich clusters, dislocation loops and nanovoids to the irradiation-induced hardening of Cu-bearing low-Ni reactor pressure vessel steels, Journal of Nuclear Materials 461 (2015) 37–44
- [17] F. Bergner, C. Pareige, M. Hernández-Mayoral, L. Malerba, C. Heintze, Application of a three-feature dispersed-barrier hardening model to neutron-irradiated Fe–Cr model alloys, Journal of Nuclear Materials 448 (2014) 96–102
- [18] J. Barthelmes, H. Hein, RPV materials behaviour: Lessons learned from microstructural results and implications regarding optimized material design, LONGLIFE Final International Workshop, 15-16 January 2014, Dresden (Germany)
- [19] M. Kirk: "Comparison of Different Embrittlement Trend Curves", IAEA Specialists' Meeting on Irradiation Embrittlement, 20th October 2010, Znojmo, Czech Republic
- [20] A. Ballesteros, E. Altstadt, F. Gillemot, H. Hein, J. Wagemans, J. Rouden, J. Barthelmes, K. Wilford, M. Serrano, M. Brumovsky, R. Chaouadi, S. Ortner, Monitoring radiation embrittlement during life extension periods, Nuclear Engineering and Design 267 (2014) 197–206



[21] E. Altstadt, Treatment of long term irradiation embrittlement effects in RPV safety assessment, Final publishable summary report, LONGLIFE D1.9 Final Report, 28 March 2014