BEHAVIOR OF SEALING MATERIALS / POLYMERS UNDER DEEP GEOTHERMAL OPERATING CONDITIONS

H. – J. Friedrich[1], R. Brüll[2], D. Zschornack[1]

[1] Fraunhofer – IKTS, [2] Fraunhofer-LBF

Förderung durch BMWi FKZ 0325904A

Content

- Introduction
- Requirements and selection criteria for sealing materials
- Experimental methods
- Laboratory test results in critical media with respect to geothermal application
- Results of in-situ-investigations with typical technical sealing materials
- Influence of nuclear radiation on polymeric materials
- Conclusions

I. Introduction

- Sealing systems are an important but oftenly underestimated part of geothermal installations
- Function: Sealing of the system internally and externally, partly also compensation of dimensional changes, damping of vibrations
- In geothermal plants typically up to several 1.000 sealings/gaskets may be in use, mostly in plate heat exchangers
- Degradation or demage of sealing material is oftenly the reason for further and also severe damages of components because of leakages or secundary material incompatibility
- The following example shows severe damage of Ti-heat exchanger plate starting with decomposition of the sealing material

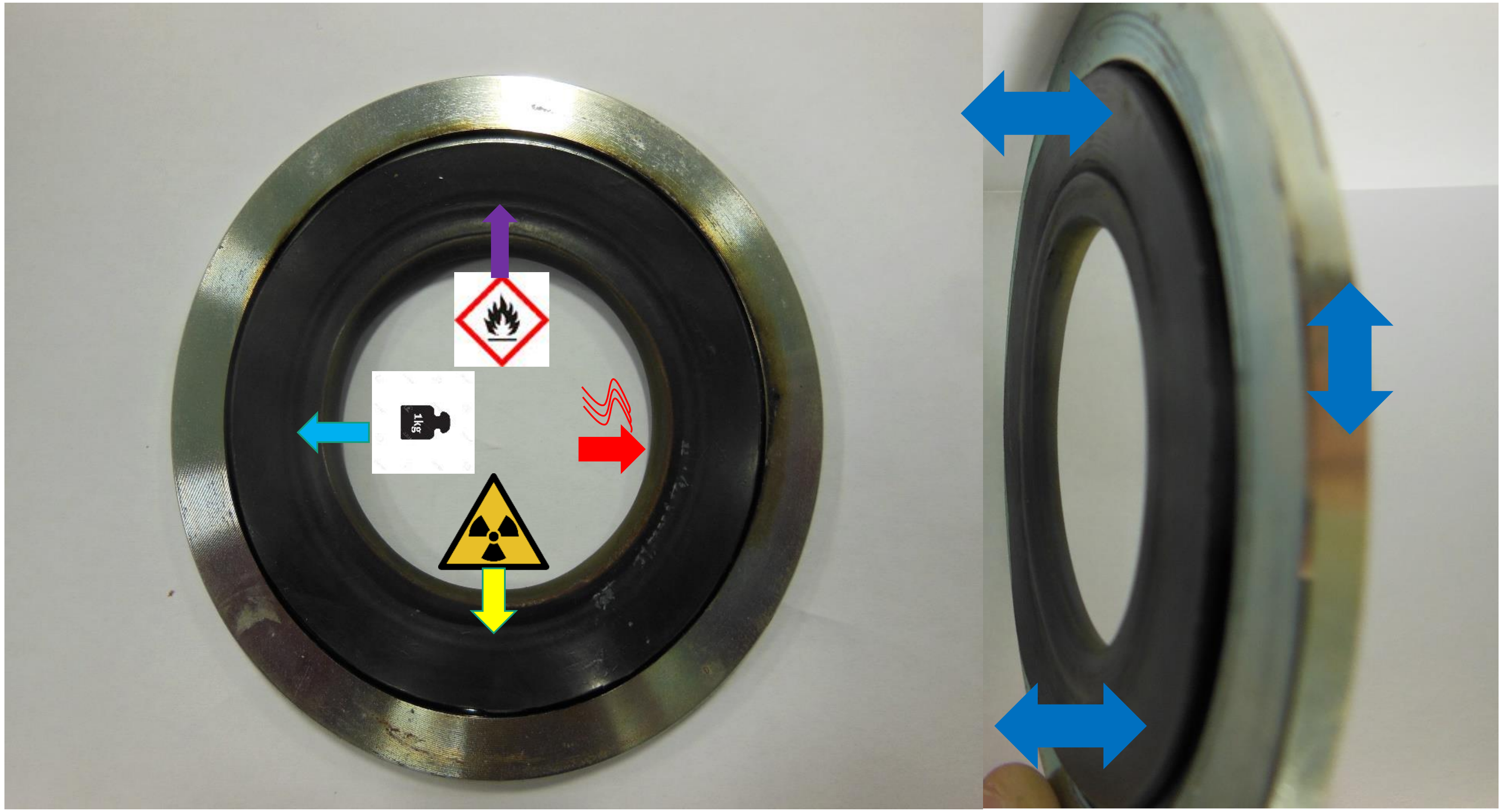
demaged sealing on Ti-plate

Severe corrosion (mispolarisation of Ti)

Typical leakage followed by corrosion

II. Requirements for sealings in deep geothermics

- In practical use the sealing /gasket material has to comply with numerous requirements: T, p, chemical attack, mechanical stresses, costs
- Can only be fulfilled with compromises



II. Requirements for gaskets / sealings in deep geothermics

- Typically material selection follows stability charts from the suppliers
- But: There are‘nt any selection guides for geothermal fluids with its more or less complex compositions
- →selection remains tricky and follows to some degree the trial and error principle
  - Technical sealing elastomers contain stabilizers with unclear behaviour (4,4‘-Dioctylphenyldiamin, Cyano-1-Hexen, Triphenylposphinoxid), which are not specified und can be extracted into the fluid phase
- Stability against radioactive radiation (Scales – NORM) may be an underestimated selection criterium
- Interaction with metallic or other piping material should also be taken into account
  - e.g. fluorinated material (FKM, FFKM, PTFE) is not recommended for direct contact to Ti
  - Graphite can provoke corrosion as well as scaling by forming local corrosion elements

→Behaviour of typical sealant material should be investigated in more detail, which is part of a recent R&D-project

II. Requirements for sealings (gaskets) in deep geothermics

List of potentially suitable materials

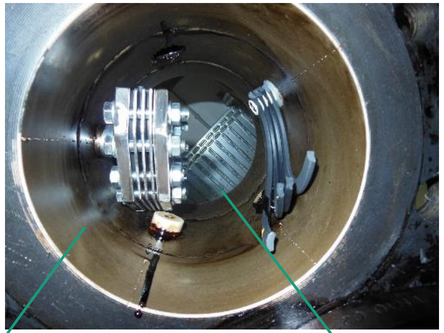
Abbrev.	Name	T_{max} °C	application	Special aspects
EPDM	Ethylen-Propylen-Dimer (sat. main chain „M“ (DIN)	150	hot water, steam	Only to recommend for the secondary cycle
NBR	Nitril-Butadien-Rubber	100	Mineral oil cont. media	
HNBR	Hydrogenised NBR	150	Dto.	less reactivity than NBR
FKM	Fluorine-Rubber -Polymerisates (Viton®)	220	good chemical resistance	partly sensitiv to hot steam, mineral oil components
FFKM	Perfluorinated Fluorine Rubber (Kalrez®)	320	very good chemical resistance	Price, incompatible to Ti
TFE	Propylen-rubber (Aflas®)	280	very good chemical resistance	price
MQ/VMQ	Methyl-Silicon /Vinyl-Methyl-Silicon	210	good chemical resistance	permability for gases
FVMQ	fluorinated Silicon rubber	175	very good chemical resistance	dimension stability, incompatible to Ti
Graphite		600	universal use	local corrosion elements possible
Metallic sealants		1500	spezific	P bis 1.000 bar

III. Methods of investigation

- Material selection for testing: EPDM, NBR, HNBR, FKM (Viton-GF)
- Reasons: practical use, performance characteristics, prices
- 1. Laboratory tests in critical media with respect to geothermal fluids (n-C_5H_{10}, n-C_7H_{16}, Kerosene, halogenated hydrocarbons, mixtures, diluted CH_3COOH)
- 2. In-situ testing
  - Neustadt-Glewe: 1060 h, 90-92°C, 7 -8 bar, Medium: high salinity, heavy metals, CH_4, N_2, CO_2, NORM, chlorinated hydrocarbons (traces)
  - Pullach: 1200 h, 102°C, 16-18 bar, Medium: low salinity, **CH_4**, mineral oil, CO_2, H_2S
- Evaluation criteria: changes in wight and dimension, shore-hardness, microscopy, DTA, DTG, IR-and mass spectroscopy

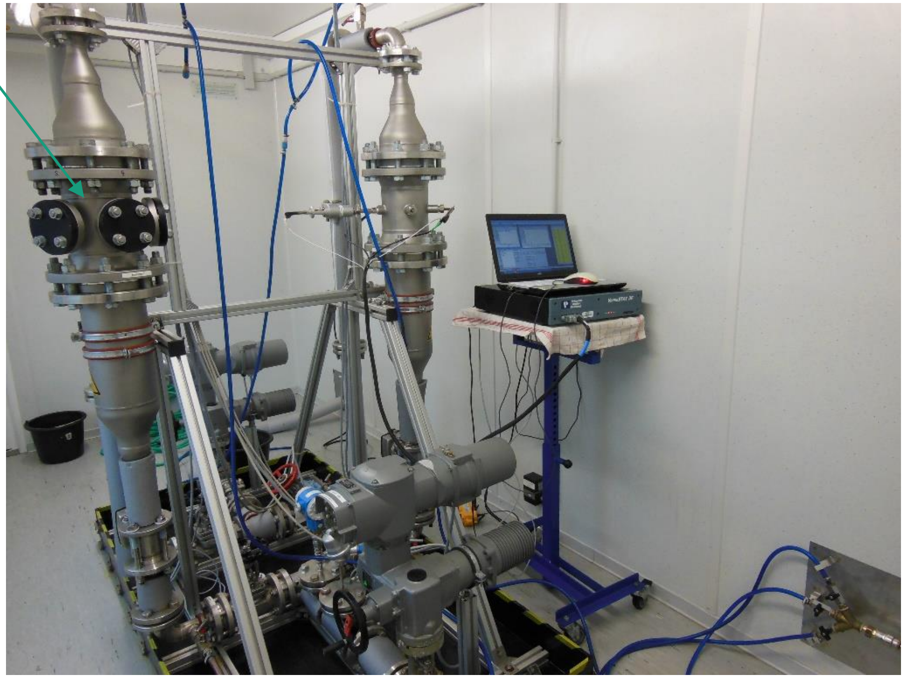
III. Methods investigation – set up for In-situ testing

Pre-pressurized with 10 Nm tightening torque



Free exposition

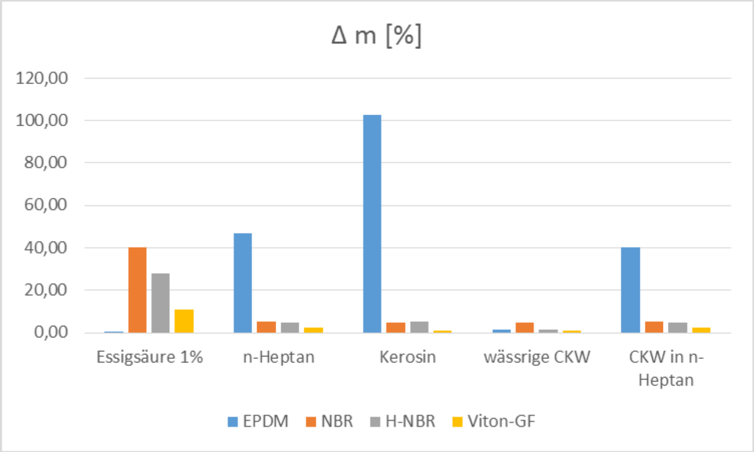
Pullach

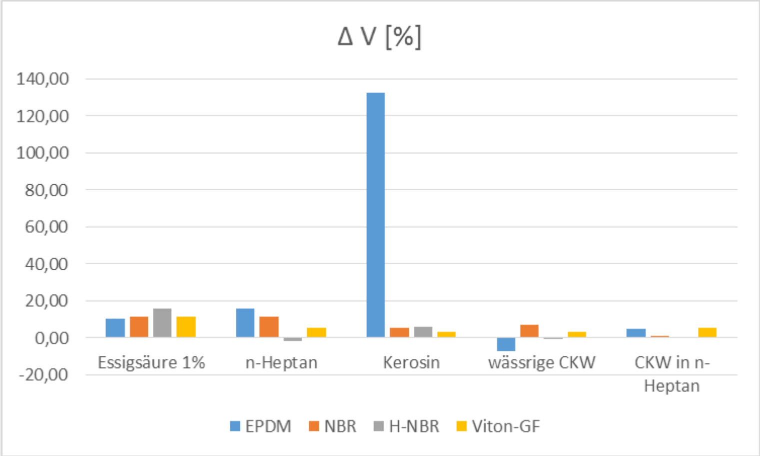


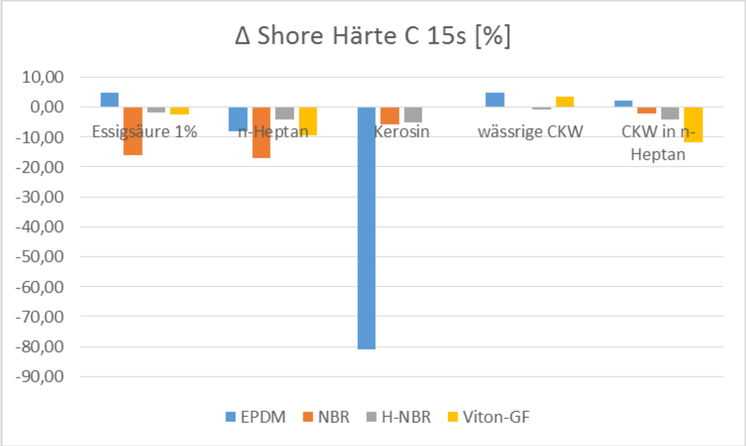
Neustadt-Glewe

IV: Results of laboratory tests

- Materials: EPDM, NBR, HNBR, FKM (Viton® GF)
- Exposition 100 h at 95 °C (+ 334 h in air)
- Media: n-Heptan, Kerosin (C_8- C_{13}-HC), LHC, acetic acid 1% (microbiell metabolism)





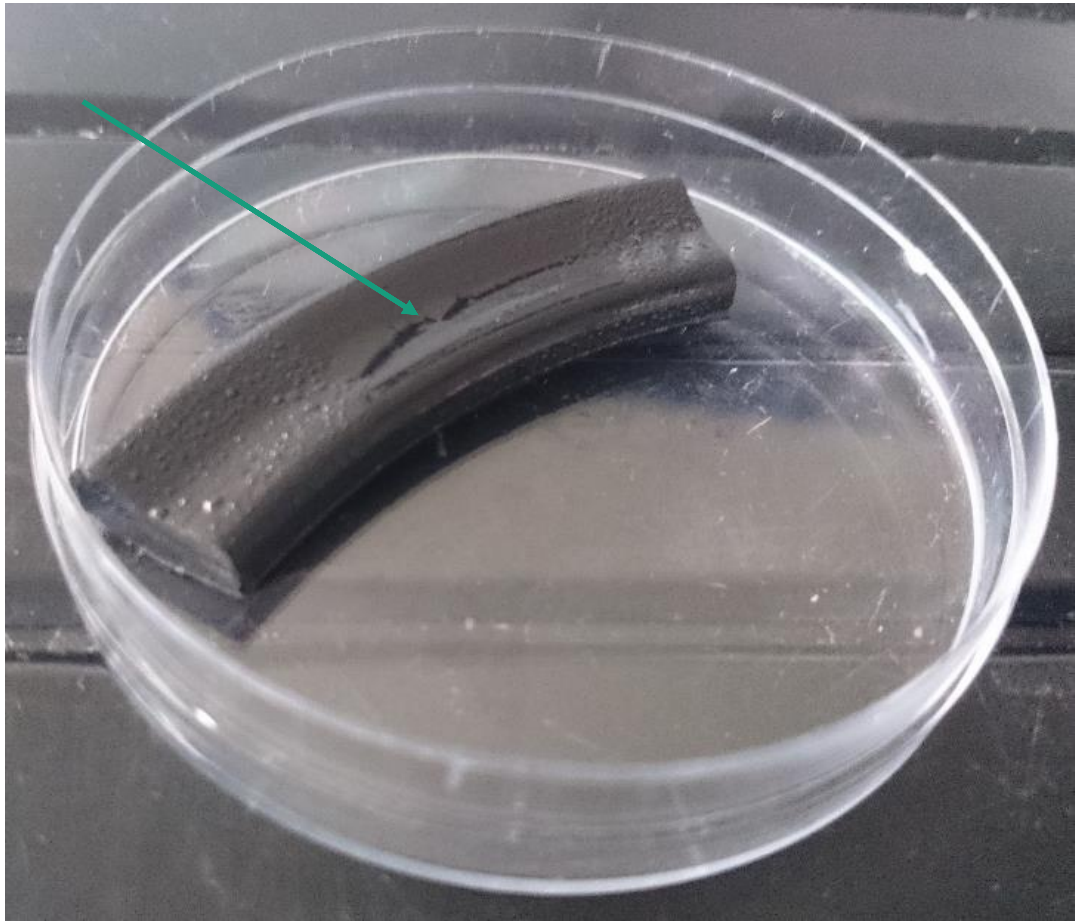


- Especially low and middle wight hydrocarbons are critical for EPDM
- High values for volume and mass excesses and also very high losses in shore hardness were observed

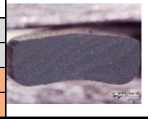
Fraunhofer IKTS

IV: Laboratory results

- Example: Degradation of EPDM in Kerosene solution with cracking



IV: Results of In-situ-exminations

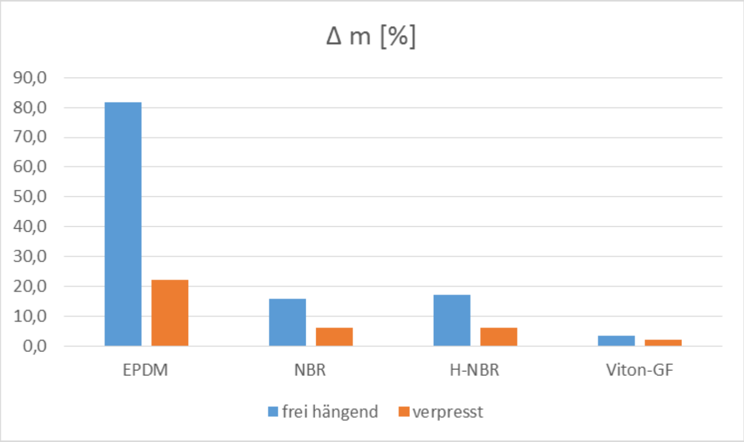
Material	Expo.-einbau	t [d]	Breite [mm]	$\overline{x}$ Dicke [mm]	Querschnittsfl. [mm^2]	Volumen [mm^3]	Gewicht [g]	$\overline{x}$ Shore-Härte C 0s	15s	Bilder Querschnitt 30x-fache Vergrößerung vorher	nachher
EPDM	frei hängend	0	10,49	3,98	40,074	7073,1	8,7750	41,7	34,3		
		50	13,64	5,25	68,440	15108,1	15,9367	28,0	25,3		
	Differenz	num.	3,2	1,3	28,4	8035,1	7,1617	-14	-9		
		%	30,0	32,0	70,8	113,6	81,6	-32,9	-26,2		
	verpresst (10Nm)	0	10,57	3,98	40,194	6210,0	7,4352	41,7	34,3		
		50	12,60	4,00	45,801	7454,1	9,0805	32,3	29,0		
	Differenz	num.	2,0	0,0	5,6	1244,1	1,6	-9	-5		
		%	19,2	0,5	13,9	20,0	22,1	-22,5	-15,5		
NBR	frei hängend	0	10,5	3,95	39,770	6979,6	9,2314	49,3	44,0		
		50	11,5	4,54	49,679	9215,5	10,6855	45,3	38,3		
	Differenz	num.	0,9	0,6	9,9	2235,8	1,5	-4	-6		
		%	8,7	15,1	24,9	32,0	15,8	-8,1	-13,0		
	verpresst (10Nm)	0	10,6	3,97	40,399	6302,2	8,0785	49,3	44,0		
		50	13,8	3,50	43,113	6876,5	8,5793	49,3	44,7		
	Differenz	num.	3,2	-0,5	2,7	574,3	0,5	0	1		
		%	30,1	-11,9	6,7	9,1	6,2	0,0	1,6		
H-NBR	frei hängend	0	11,0	4,11	40,374	7226,9	9,5390	50,7	44,3		
		50	11,7	4,50	46,852	8855,0	11,1807	55,3	49,0		
	Differenz	num.	0,7	0,4	6,5	1628,1	1,6	5	5		
		%	6,3	9,6	16,0	22,5	17,2	9,1	10,6		
	verpresst (10Nm)	0	10,7	4,02	38,214	6037,8	8,3474	50,7	44,3		
		50	14,0	3,19	40,863	6752,6	8,8520	52,7	49,7		
	Differenz	num.	3,4	-0,8	2,6	714,8	0,5	2	5		
		%	31,7	-20,6	6,9	11,8	6,0	3,9	12,2		
Viton-GF	frei hängend	0	10,5	4,05	40,413	6799,5	13,4923	47,3	42,0		
		50	10,7	4,25	43,922	7631,4	13,9323	46,7	39,7		
	Differenz	num.	0,3	0,2	3,5	832,0	0,4	-1	-2		
		%	2,4	5,0	8,7	12,2	3,3	-1,3	-5,5		
	verpresst (10Nm)	0	10,5	3,90	40,453	6330,9	12,5560	47,3	42,0		
		50	11,1	3,08	44,746	7192,9	12,8069	42,7	38,3		
	Differenz	num.	0,6	-0,8	4,3	862,0	0,3	-5	-4		
		%	5,4	-21,0	10,6	13,6	2,0	-9,7	-8,8		

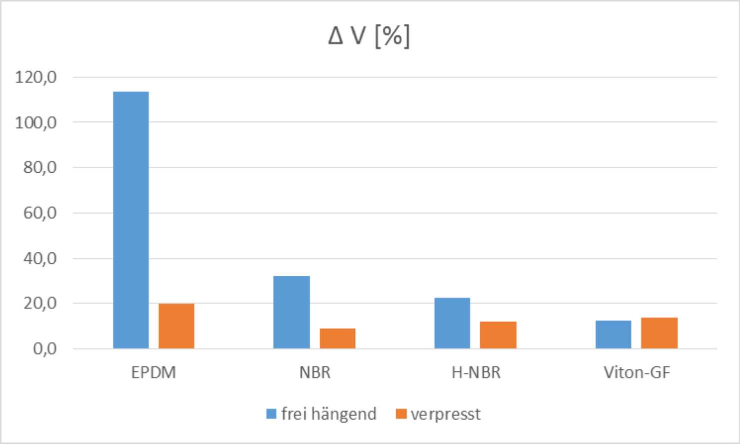
example
detailed analysis
exposition test
at Pullach
Checked were
changes in
-dimension
-volume
-mass
Shore hardness

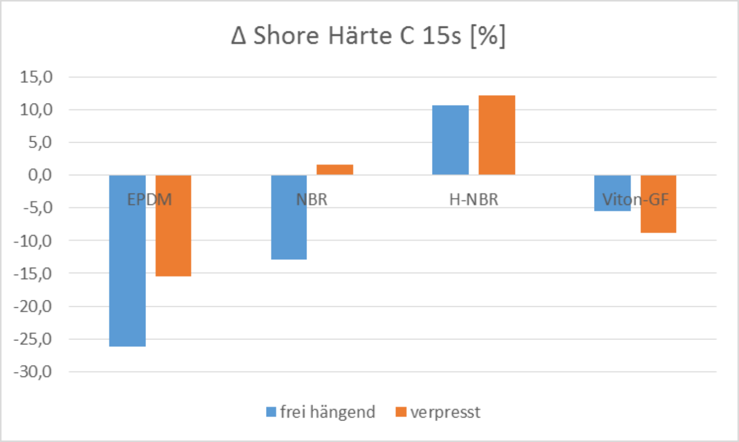
Fraunhofer IKTS

V. In-situ-Exposition – evaluation of mechanical properties

- Results Pullach







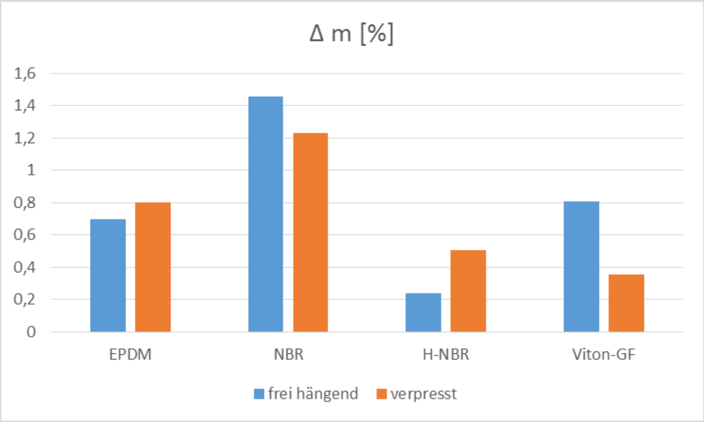
- EPDM shows large changes in mass and volume, NBR, HNBR only slight ones
- Excluded HNBR reduction in shore hardness is observed, EPDM strong reduction

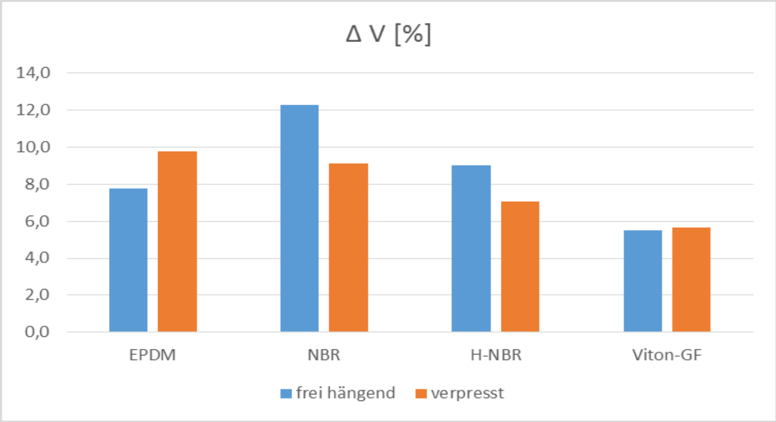
→ EPDM as sealant material in such fluid not suitable

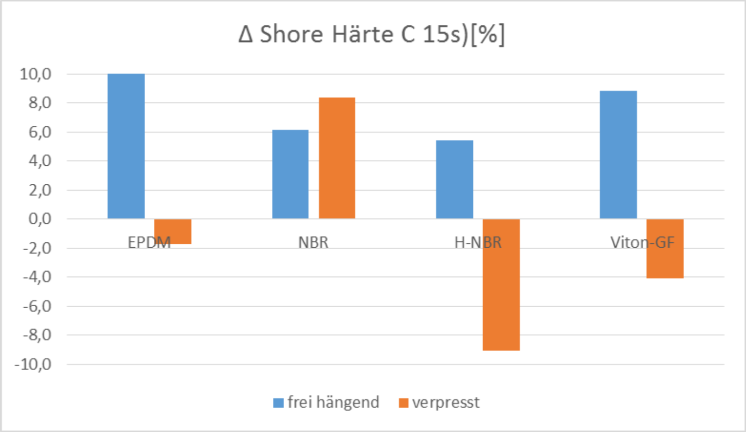
Fraunhofer IKTS

V. In-situ-Exposition – In-situ-Exposition – evaluation of mechanical properties

- Results Neustadt-Glewe





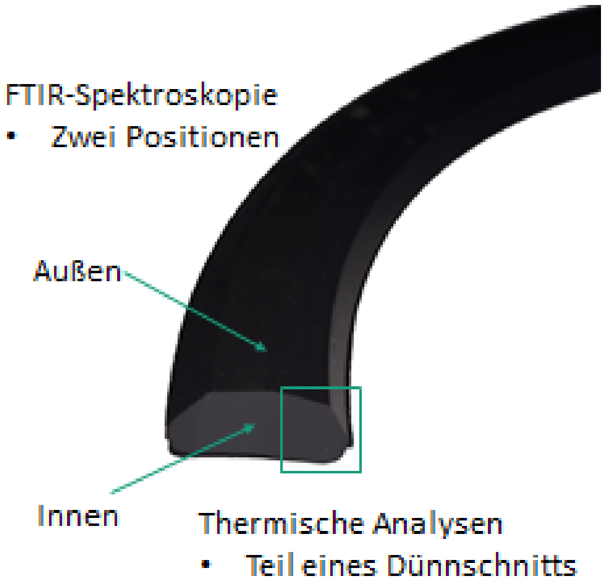


- In general only slight changes in mass and volume or shore hardness

VI. More detailed examinations

- DSC, DTG + Mass-Spectroscopy

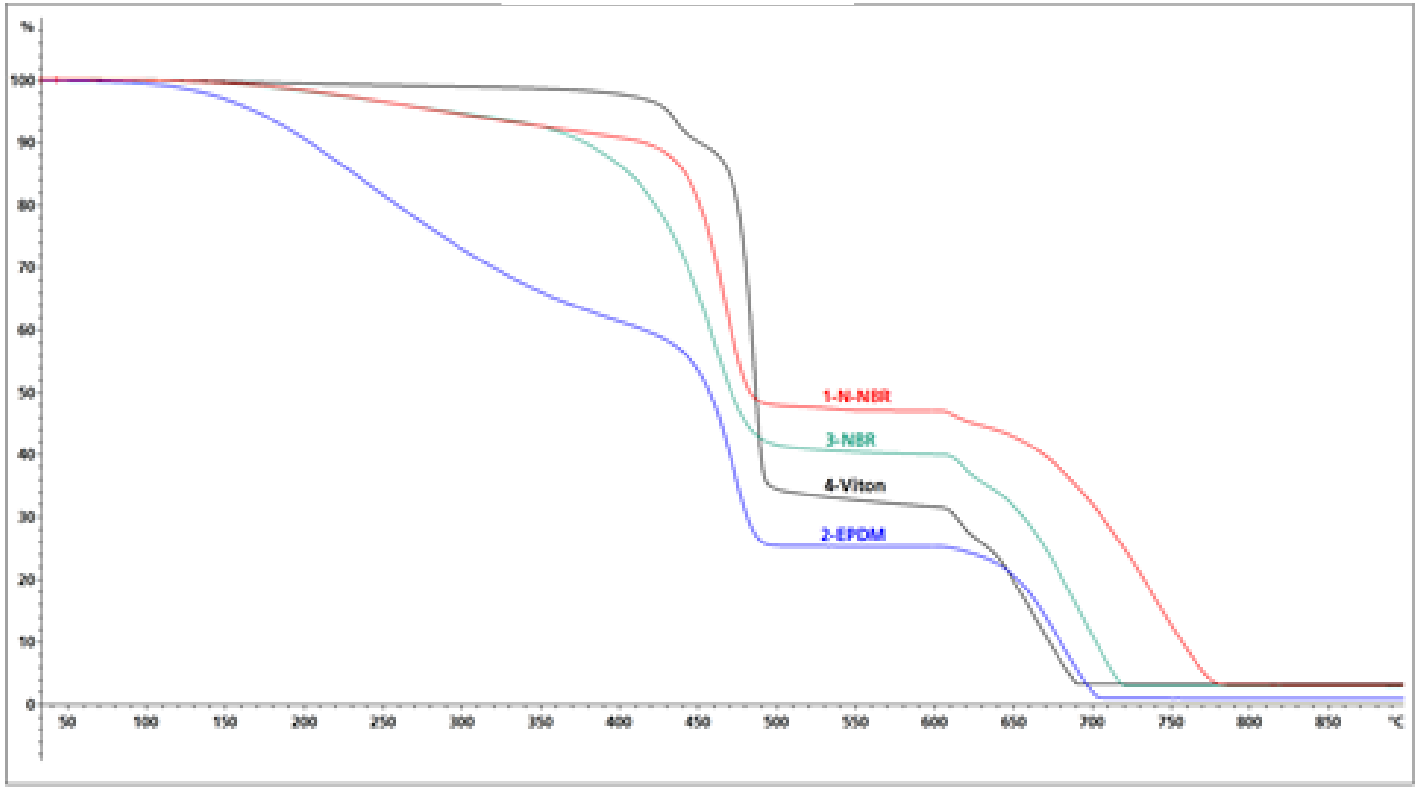
Experimentelles



- DSC
  - -100 – 300 °C ; 10 K/min
    2_Zyklen
- TGA
  - 35 – 600 °C ; 10 K/min N_2
  - 600 – 900 °C ; 10 K/min Luft
- FTIR-Spektroskopie
  - ATR
  - 16 Scans pro Spektrum mit einer spektralen Auflösung von 4 cm^{-1} akkumuliert

VI. Results of more detailed examinations

results for DTG (differential thermo gravimetry) after Exposition Pullach



Medieneinfluss auf das thermische Zersetzungsverhalten wird mit Referenzproben untersucht.

→ EPDM lowest thermal stability , Ranking: Viton®-GF, HNBR, NBR, EPDM

VI. Results of more detailed examinations

- Results Pyrolysis-GC-MS from exposed and from HNBR as delivered

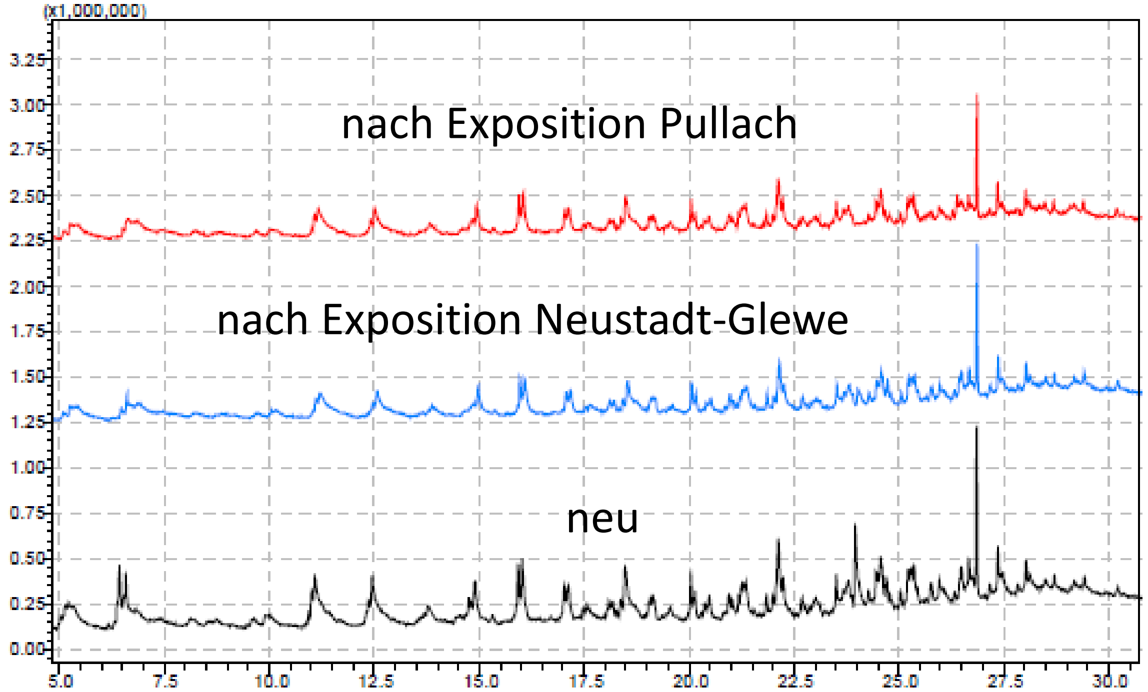


Abbildung 26 Total Ionen Chromatogramme (SCAN: 15-500 Da) der Proben HNBR Nr. 05 (Pullach, rot), HNBR Nr. 15 (Neustadt, blau) und HNBR Nr. 19 (unbelastet, schwarz), Ausschnitt 5 – 31 min

→ In case of HNBR no significant alterations in its mass spectrum – indicating no attack

VI. Results of more detailed examinations

- Results Pyrolyse-GC-MS for exposed and EPDM as delivered

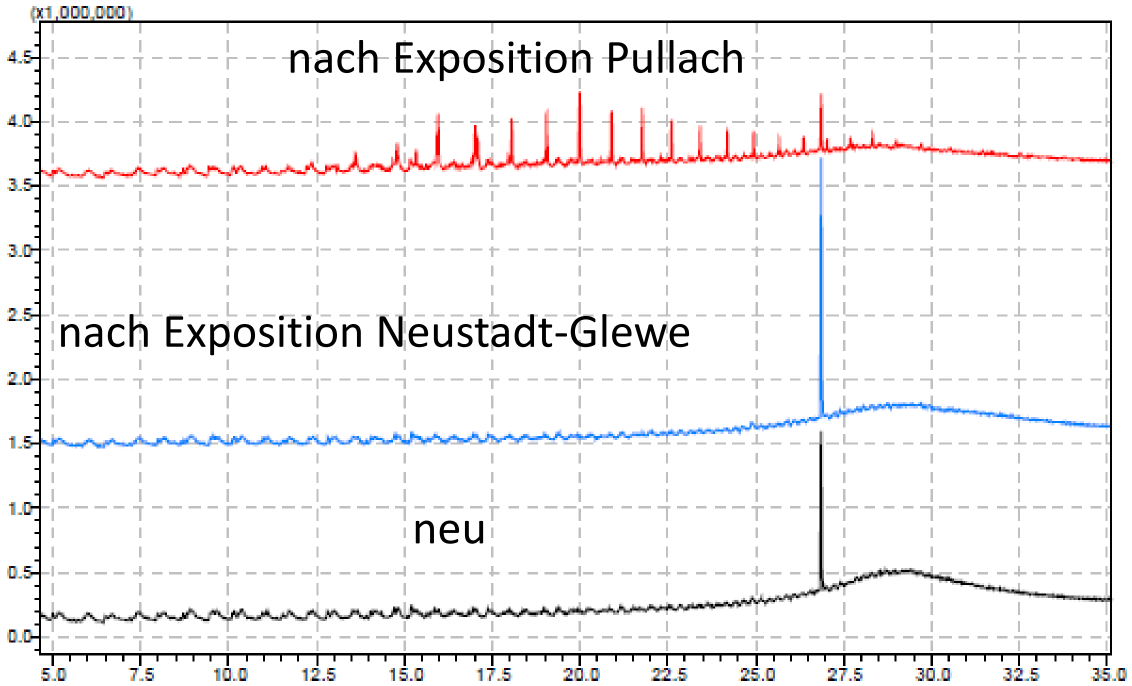


Abbildung 35 Total Ionen Chromatogramme (SCAN: 15-500 Da) der Proben EPDM Nr. 06 (Pullach, rot), EPDM Nr. 16 (Neustadt, blau) und EPDM Nr. 20 (unbelastet, schwarz), Ausschnitt 5 – 35 min

→ For EPDM significant changes in its mass sprectrum,

→ Indicates leaching of stabilizers and infiltration of higher hydrocarbons

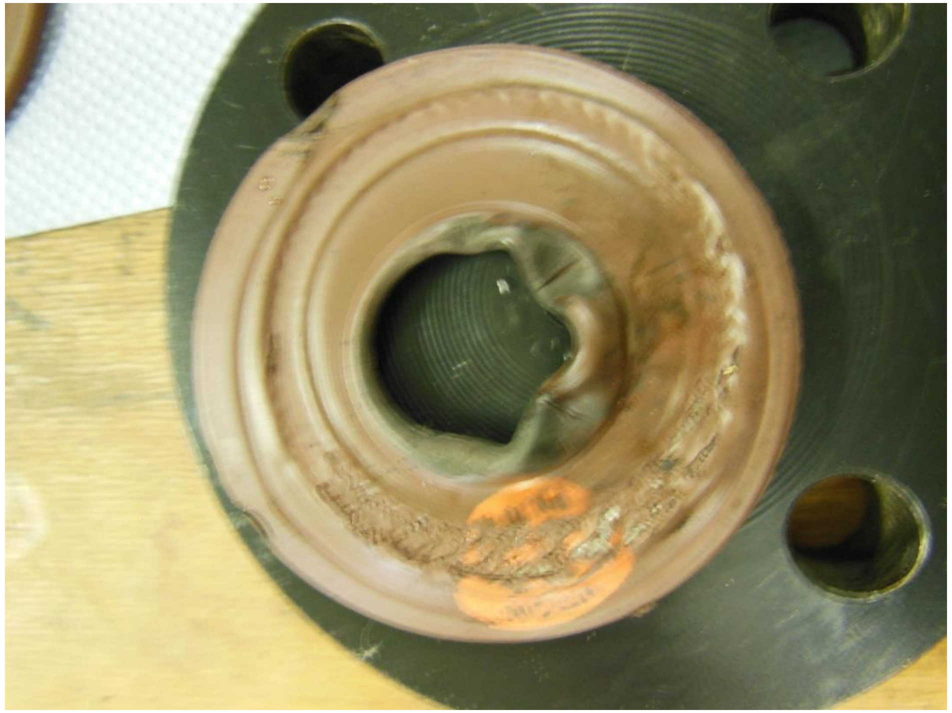
VI. Results of more detailed examinations – summary of results

Methode	Results (score)	
	Neustadt-Glewe	Pullach
Thermal Stability (DTG, DTA)	EPDM ↓	EPDM↓↓
	NBR →	NBR→
	HNBR↑	HNBR↑
	FKM↑↑	FKM↑↑
Chemical stability (Pyrolyse-GC-MS, FTIR-ATR, leaching/decomposition of stabilizers Absorption of MHC	EPDM ↓	EPDM↓↓
	NBR →	NBR→
	HNBR↑↑	HNBR↑↑
	FKM↑↑	FKM↑↑
Phase transitions (indication of physical degradation)	EPDM ↓	EPDM↓↓
	NBR ↑	NBR↑
	HNBR↑	HNBR↑
	FKM↑↑	FKM↑↑

Ranking: 1. FFKM, 2. HNBR, 3. NBR, 4. EPDM (not to recommend)

VI. In-situ-Exposition – other remarkable findings

- Pullach: strong absorption of gases, de-gassing after pressure reduction, may be a reason for ruptures



Viton-gasket from exposition chamber after 1220 h!
→type of material also of great influence

VI - Influence of nuclear radiation on polymeric materials

- Practical findings for Neustadt-Glewe can‘t be explained sufficiently by our analytical results→looking also for other factors
- Thermal brines (North German bassin, upper Rhine trench) contain natural radionuclides (NORM)
- Specific activity in the liquid phase very low, typical range is mBq/l
- <u>But:</u> strong accumulation in Scales (…x*10^2 Bq/g) over longer periods of time
- Dose rate ca. 5-10 µSv/h in 10 cm distance, known quadratic correlation between distance and locally received energy $E_l \sim 1/r^2$
  - →directly on material surfaces very high radiation doses will be possible (kGy)
  - →over longer time intervalls those are sufficient to damage polymeric materials
- Some typical limits for radiation damage (Gy = J/kg) in air, measured for Co-60 (γ-radiation, 1,17/1,33 MeV) (Source: CERN, Grenoble)
  - Polyesters 1..10 MGy
  - Epoxy resins …1 MGy
  - PVC, Elastomeres 0,05-0,1 MGy
  - <u>PTFE 0,005 MGy – may be a reason for rapid scaling at PTFE-liners</u>

VI - Influence of nuclear radiation on polymeric materials

- Energy of nuclear radiation in comparison to typical energy of chemical bonds

Nuklid	α MeV	β keV
Pb-210	-	64
Po-214	5,407	-
Rn-222	5,59	-
Ra-226	4,87	
Ra-228	-	46

Bindungsart	Bindungsenergie ev
C-H	3,52
C-H-N	5,29
CH2	4,46
CN	7,92
CF	5,65

→Energy of nuclear radiation exceeds chemical bonding energy by a factor of 10^4 (β-) …

10^6- (α-particles),

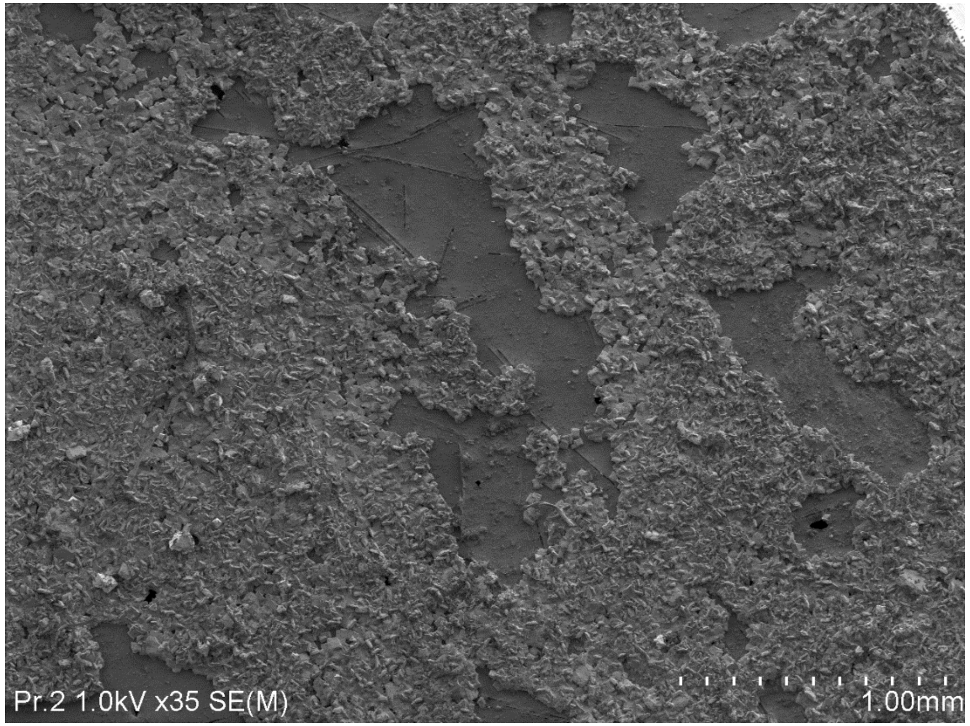
→radiation demage will be possible

→In agreement with practical experience from other sectors (nuclear technology, radiochemistry, sterilisation of medical products, therapy of cancer)

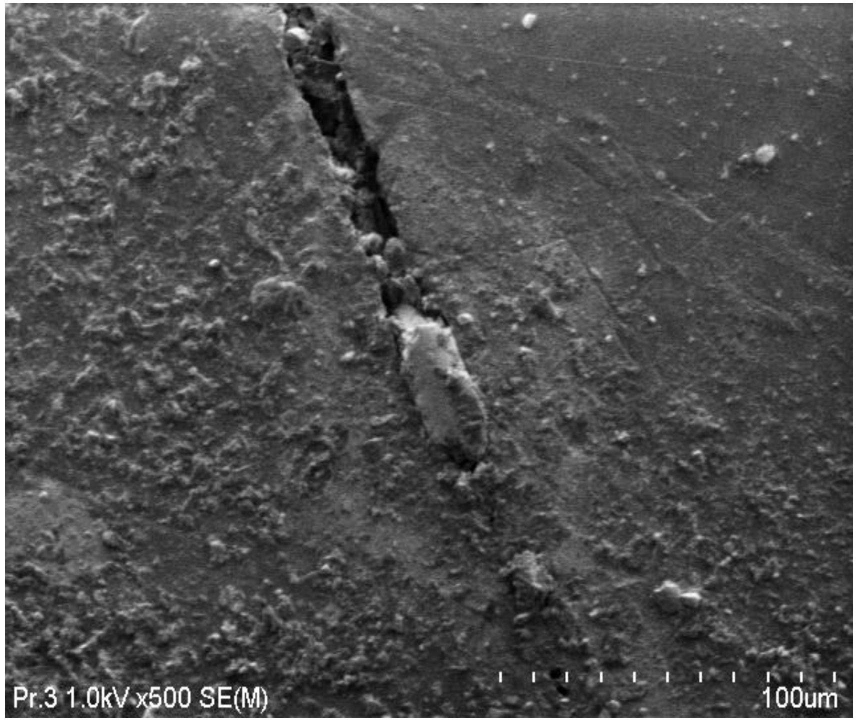
→Hence this mechanism of damage is also plausible under geothermal conditions!

VI - Influence of nuclear radiation on polymeric materials

- Examples from practice…



Formation of cracks under lead scale in fiber armed Epoxy resin („GfK“)



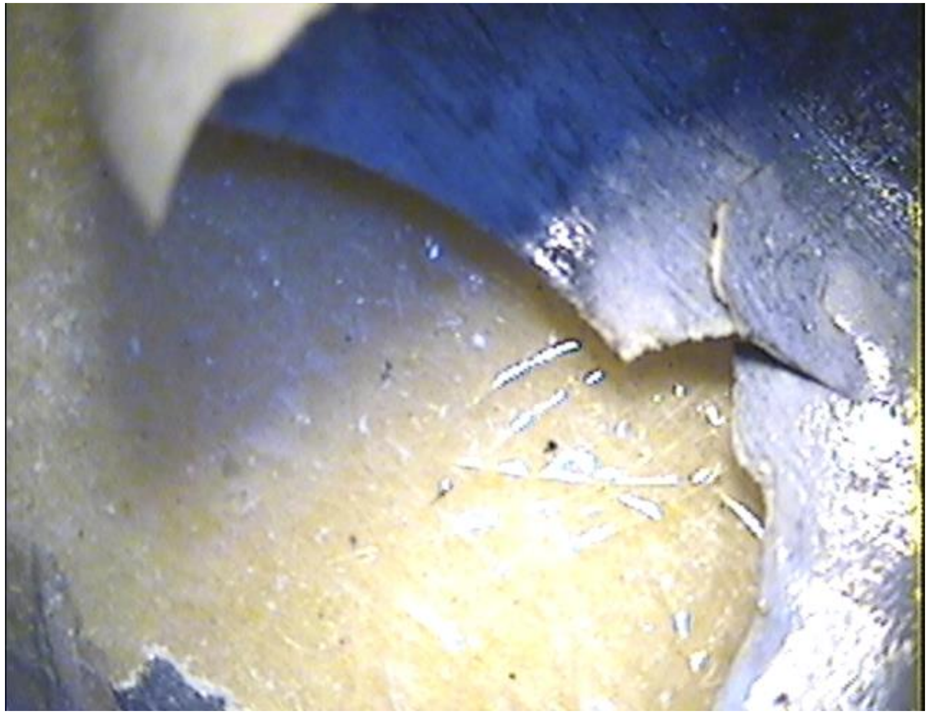
Formation of scale within cracks

- Radioactive Scale seems to induce degradation of polymeric matrix starting from surficial attack ore pores

VI Influence of nuclear radiation on polymeric materials

- Further findings from practice…

Destroyed gasket, EPDM (with scaling)



Severe damage of fiber-armed Epoxy

- Numerous indications for contribution of radiation to degradation mechanism of polymeric materials
- Urgent need for deeper insight to ensure long-time integrity of plant components!

VII - Conclusions

- The selection of sealing materials requires detailed knowledge of the operating conditions

  with respect to chemical composition of the fluid, temperature and pressure states
- Critical components in geothermal fluids with respect to material selection are especially hydrocarbons including CH_4, lower chlorinated hydrocarbons and probably the formation of scales containing elevated concentrations of NORM
- Significant damage mechanism is the leaching (extraction) of stabilizers and penetration of hydrocarbons in the elastomer matrix
- HNBR and FKM/FFKM showed good and very good resistance in our In-situ exposition tests
  - But: FKM/FFKM can induce Corrosion when in contact to Ti-alloys
- EPDM proved unsatisfactory for use in contact to geothermal fluids
- Indication for a radiation damage are plausible but further work is necessary for better understanding of the mechanism and improvement of materials

- Vielen Dank für die Aufmerksamkeit

- Vielen Dank an PtJ und BMWi für die Förderung