Unexpected Accumulation of Naturally Occurring Radionuclide's in a Petrochemical Plant

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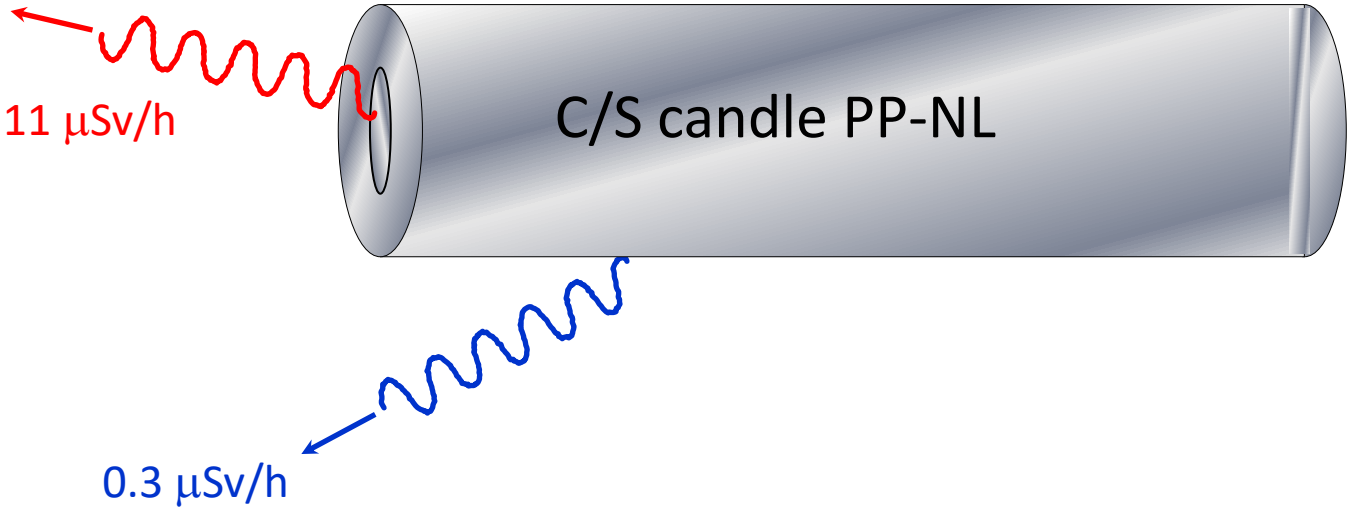
Unexpected Accumulation of NOR's in a Petrochemical Plant

Events

- Container with scrap of a Polyol Plant (PP-NL) triggers portal monitor alarm at Scrap Dealer.
- Notification of VROM-Inspection Region South-West.
- Contractor investigation of contents of PP-NL scrap container (dose rate outside container 0.15 μSv/h at maximum).
- Approval from VROM to transport a C/S candle to SRTCA for investigations

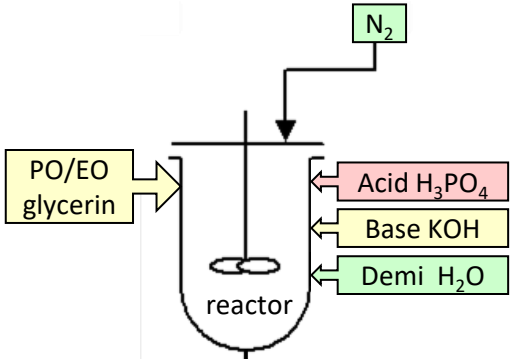
Coalescer/Settler (C/S) Candles

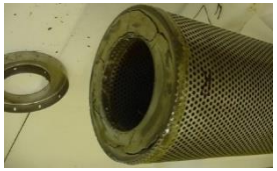
C/S Candle β/γ External Radiation

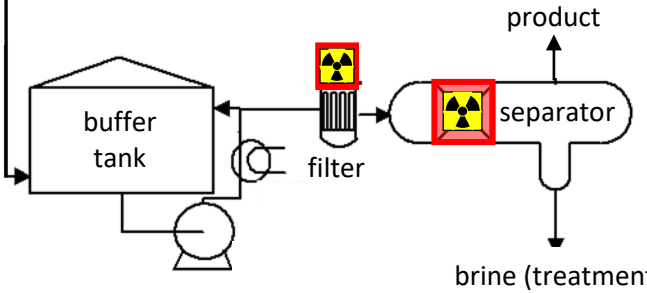


Polyol Plant NL

Simplified Flow Scheme Plant (partly)

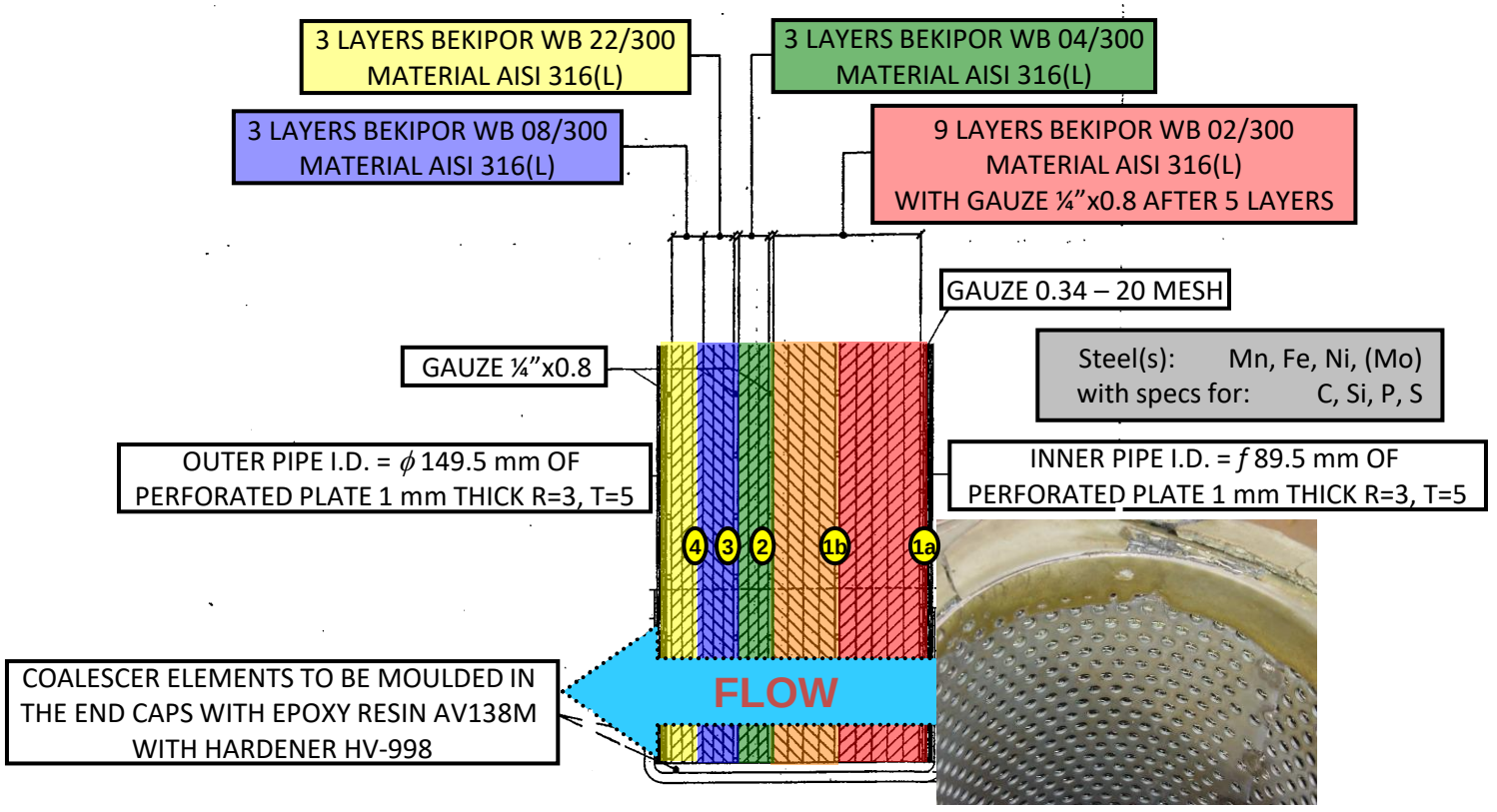






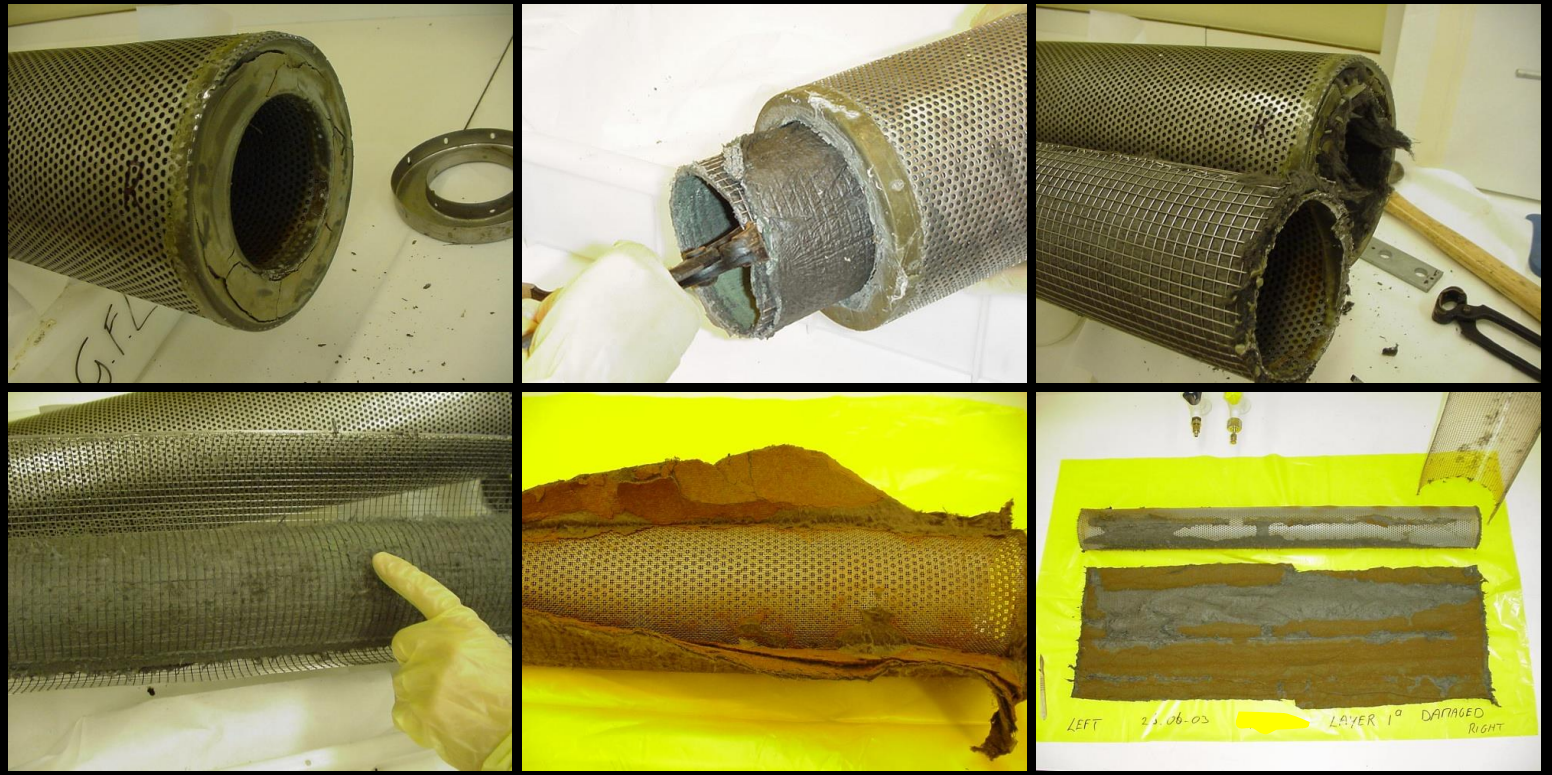
C/S Candles

Construction and Operation



Polyol Plant NL

Controlled Dismantling C/S Candle



Grab Sample Deposits, ex C/S Candles PP-NL

Gamma-Spectroscopic Analysis

identification and quantification of Naturally Occurring Radionuclides (Bq[NOR]/g)

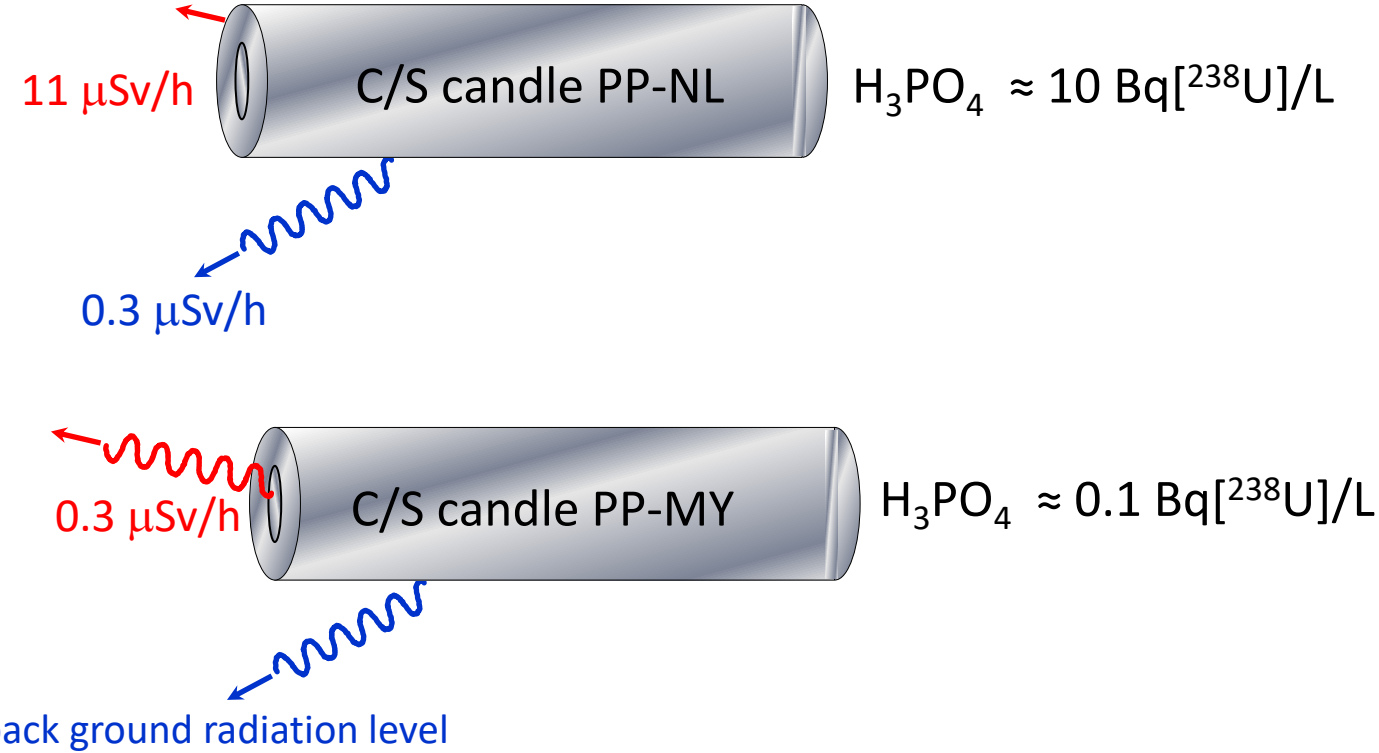
^{40}K	1.5				
^{232}Th	< det lim*)	^{228}Ra	< det lim#)	^{228}Th	< det lim#)
^{235}U	**24**	^{227}Ac	0.5	^{223}Ra	0.5
^{238}U	**520**	^{226}Ra	< det lim#)	**^{210}Pb**	**29**

*) detection limit XRF

#) detection limit gamma-spectrometry

C/S Candle Contamination

C/S Candle β/γ External Radiation



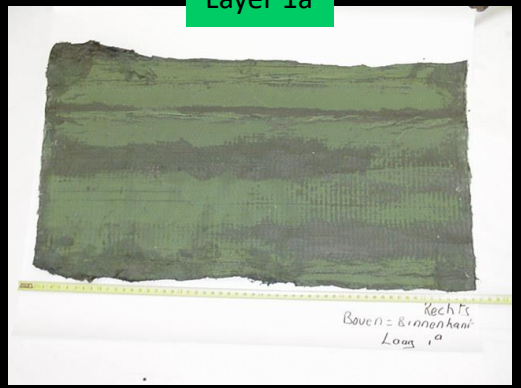
Polyol Plants: NL (top row) **& MY** (bottom row)

Controlled Dismantling C/S Candle

Layer 1a

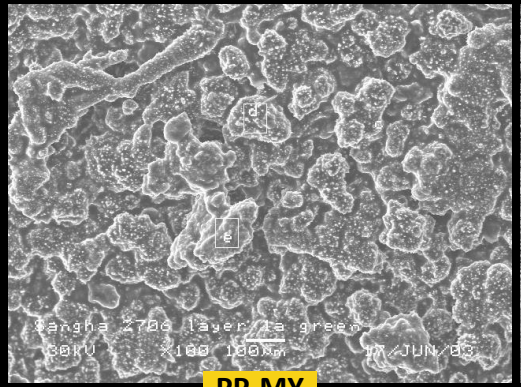
Layer 1a (detail)

Layer 1b

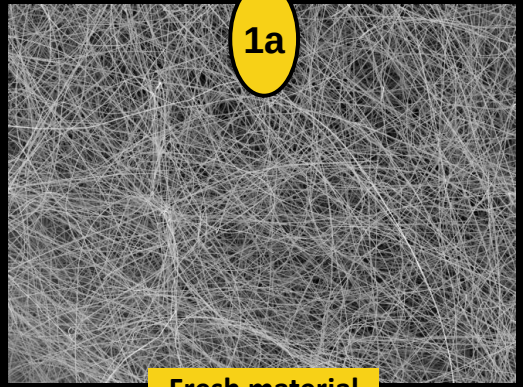


Polyol Plants NL & MY

SEM Images – Used & Fresh C/S Candle



PP-MY



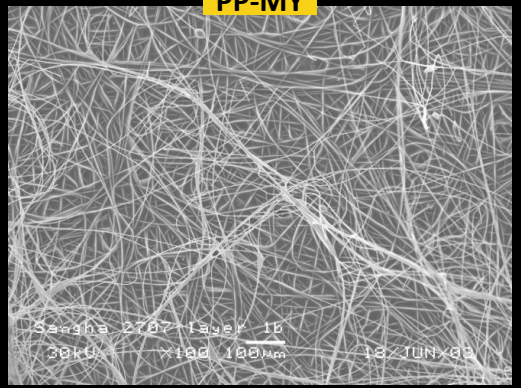
1a

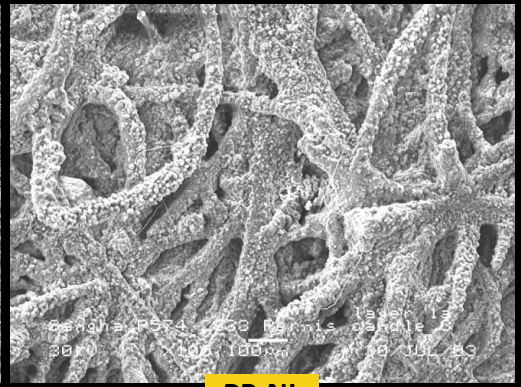
Fresh material

Magnification 100 ×

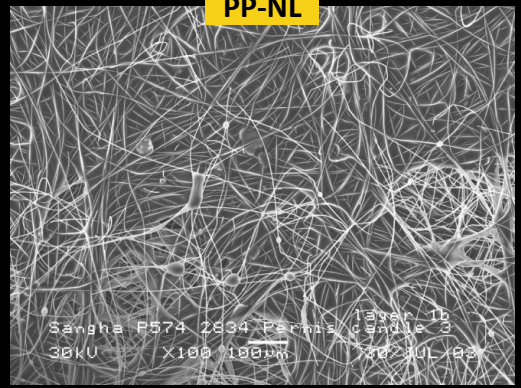
1b

↔ = 100 µm





PP-NL



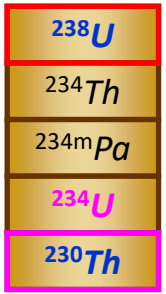
C/S Candle Contamination

NOR distribution over filter matrasses

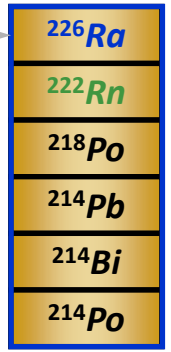
	NOR total activity kBq	Distribution of Naturally Occurring Radionuclide (NOR) layer 1a	layer 1b	layer 2	layer 3	layer 4
PP-NL						
^{238}U	316,6	96,3%	2,8%	0,4%	0,2%	0,1%
^{234}U	310,7	96,2%	3,5%	0,4%	0,0%	0,0%
^{226}Ra	0,2	100,0%	0,0%	0,0%	0,0%	0,0%
^{210}Pb	15,7	98,8%	1,1%	0,1%	0,0%	0,0%
^{235}U	14,9	96,8%	2,6%	0,4%	0,1%	0,0%
PP-MY						
^{238}U	1,86	100,0%	0,0%	0,0%	0,0%	0,0%
^{234}U	2,02	100,0%	0,0%	0,0%	0,0%	0,0%
^{226}Ra	< det lim					
^{210}Pb	0,01	100,0%	0,0%	0,0%	0,0%	0,0%
^{235}U	0,09	100,0%	0,0%	0,0%	0,0%	0,0%

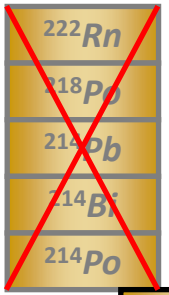
Phosphoric Acid Production

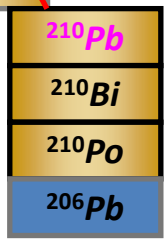
Phosphate Rock (wet or thermal processing)



If a "system" is not closed to radionuclide migration (*e.g. ground phosphate rock during processing/digesting*), the secular equilibrium may become disturbed. A migrated *daughter* nuclide (*226Ra*) may start a decay series for its own in its own preferred environment (*aqueous waste streams*), so-called ***sub-series*** will be formed.







NOR's encounter for Phosphate Industry (wet process)

		^{238}U	^{230}Th	^{226}Ra	^{210}Pb
Products:	NPK Fertilisers	y	y	y/n	y/n
	Phosphoric acid	**y**	**n**/y	n/y	n/**y**
Waste:	Phosphogypsum	n	n	y	y
	Aqueous streams	n	n	y	y
	Stack	n	n	n	y

Phosphoric Acid (PA) Production

Phosphate Rock (wet > phosphogypsum or thermal > via elemental P)

Supplier Manufacturer	H_3PO_4	Origin of sample	PA process	Grade type	Element (ppb)			
					Ti	Zr	Th	U
A	75%	supplier	wet	technical	1500	250	< 5	77
	75%	PP-NL	wet	technical	2150	230	< 5	70
	85%	supplier	wet	technical	2240	18		
	85%	supplier	wet	technical	2340	23	3	870
B	75%	supplier	wet	technical	2500	4130	< 5	440
	75%	PP-NL	wet	technical	4420	3210	< 5	1080
	85%	supplier	wet	technical	4060	4650	< 5	450
	85%	supplier	wet/+?	food	4470	4030	3	2040
	85%	supplier	wet/+?	food	4275	3630	5	1800
C	85%	PP-MY	wet/filter	food	14	7	7	< 5
	85%	supplier UK	wet/filter	food	120	170	< 5	8
	85%	supplier UK	wet/filter	food	110	160	< 2	3
D	75%	supplier NL	wet/filter	food	140	6	2	< 2
E	85%	PP-MY	wet/filter	food	190	21	6	1
F	75%	PP-NL	thermal	food	580	38	8	< 1
G	85%	supplier PRC	wet/filter	food	275	30	4	< 1
H	85%	PP-MY	wet/+?	food	1100	30	2	1
	85%	PP-MY	wet/+?	food	2700	400	1	42
I	85%	PP-MY	wet/+?	food	1200	12	1	< 1

C/S Candle Contamination – Deposit Analysis

deposit XRF analysis Z	Symbol	M_A	PP-NL w%	PP-MY w%	(most likely) originating from
15	P	31	10,5%	9,5%	H_3PO_4
19	K	39	11,5%	9,5%	KOH
22	Ti	48	4,5%	4,5%	H_3PO_4 impurity
24	Cr	52	2,5%	3,5%	AISI 316 L
26	Fe	56	22,5%	32,5%	AISI 316 L
28	Ni	59	1,0%	1,0%	AISI 316 L
40	Zr	91	4,0%		H_3PO_4 impurity
92	U	238	7,0%	0,9%	H_3PO_4 impurity
XRD morphology					
$K_2Ti_2(PO_4)_3$			Bulk	2nd phase	KOH/H_3PO_4
$KTiOPO_4$			2nd phase	3rd phase	KOH/H_3PO_4
$KFe_2(OH)(PO_4)_2(H_2O)_2$				Bulk	KOH/H_3PO_4
Fe (metal)			3rd phase		AISI 316 L
Cr (metal)			4th phase		AISI 316 L
FeNi (alloy)			5th phase		AISI 316 L
$(UO_2)HPO_4(3\text{-}x)H_2O$			trace		H_3PO_4 (imp)

Conclusions, Recommendations and Scope for PP-NL

Radiological License to Operate, Change PA Grade and Clearance

Conclusion

- U_{nat} impurities in phosphoric acid root cause for 'radioactive' deposits inside spent C/S candles
- Differences Spent C/S Candles from PP-NL and PP-MY:
  1. U_{nat} contents in PP-MY Candles substantially less than in PP-NL Candles
  2. PP-MY deposit texture very different from that in PP-NL candles
  3. Impurities/Impurity levels in Phosphorous Acid significantly different for PP-MY ('food grade') and PP-NL ('technical grade').
- PP-NL spent C/S candles classified as 'radioactive waste' and require licensing

Recommendation

➢ Change to food grade phosphoric acid
  - define impurity specifications for Ti, Zr, Th and U
  - control/monitor phosphoric acid intake (physical data base)

Scope

☺ C/S candles cleared from 'radioactive control regime' (proof/notification to competent authority)
☺ longer operational life time of C/S candles
☺ ultra-sonic cleaning of C/S Candle for regeneration (*cf*. PP-MY)

Dose Assessment C/S Candle Contamination

various handlings with C/S Candles

Worker Location	Operation	Workers	Assessed Doses (µSv) external	internal	total	natural background
SRTCA	C/S Candle Transport PP-NL > SRTCA, incl. Regeneration Trials	2	0,1	-	0,1	6%
SRTCA	Cutting a C/S Candle Open for Demonstration Purposes, incl. Internal Transport and Storage in Office	1	1	5	6	6%
		2	1	-	1	
		1	0,3	-	0,3	
PP-NL	Candle Exchange in C/S Unit for Optimal Plant Operation	3	0,3	-	0,3	77%
PP-NL	Filter Exchange in Terrace Filter Unit for Optimal Plant Operation	4	1,5	-	1,5	460%
PP-NL	Cutting a C/S Candle Open for Deposit Sampling	2	2	5	7	89%
PP-NL	Sample Analysis at the Production Laboratory	2	0,5	4,5	5	32%

Conclusions from a Radiological Point of View

- Dose assessment fully focused on the SRTCA and PP-NL workforce

- Handlings with C/S Candles containing U_{nat} contaminated deposits do not give rise to doses exceeding the negligibility dose limit (10 µSv/a)
  - apart from awareness no other measures from an HSE point of view required.

- a more comprehensive assessment should track the follow-up route of the U_{nat} contaminated Spent C/S Candles
  - scrap handling (scrap yard workers),
  - route of U_{nat} (and ^{210}Pb) during melting (melting plant workers)
  - any subsequent public and environmental exposure

- from a nuclear energy act point of view (fissionable material) a radiological license is required, but it would be questionable, if such a license would be required from a dose point of view