Polymeric materials in a nuclear power plant from a radwaste point of view

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Background

- SKB, the Swedish Nuclear Fuel and Waste Management Company, has in recent years performed thororugh investigations regarding complexing agents in SFR
- The result was stricter limits in the waste for some substances, and milder for other
- The Swedish Radiation Safety Authority did not approve the new acceptance criteria (more time for evaluation was needed)
- Meanwhile, SKB has issued a temporary regulation
- At the moment, there are very strict requirements (for each complexing agent, the strictest limit is chosen from the two sets of acceptance criteria)
- We also have requirements on some polymeric materials, since their degradation products can be classified as complexing agents



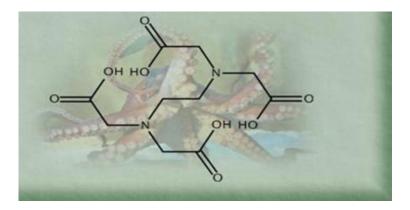
What is a complexing agent?

- Normally found in soaps, detergents etc.
- The main task is to bind calcium and magnesium ions in washing water, i.e., to soften hard water.
- E.g. EDTA, NTA, zeolites, citric acid
- From a radwaste point of view, strong organic complexing agents are of primary concern.

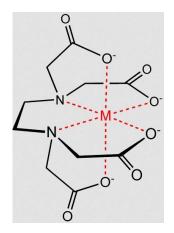


What is a complexing agent?

Structures remind of an Octupus



The arms grab a metal ion





Why of intrest in SFR?

- Radioactivity outflow from the repository must be slow
- Radioactivite substances (metal-ion radionuclides) are often poorly soluble in water, and sorb to solid materials such as cement
- Complexing agents make the radionuclides more soluble, meaning faster outflow with the groundwater from the repository
- An analogy can be made with amusement park machines:





Todays requirements- part 1(2)

Tabell 3-1. Gränsvärden för koncentrationer av lösta komplexbildare, och mängder av material som kan brytas ner till komplexbildare.

Material	Ämne/Ämnesklass	Övre gränsvärde ^a	
Cellulosa	Isosackarinat (ISA)	10 ⁻⁴ M ^{b,c}	
Hygien, tvätt, rengöring, dekont.	Oktadentata karboxylerade triaminer, t ex dietylentriaminpentaacetat	Förbjudet	
	α-hydroxikarboxylater, t ex glukonat	Förbjudet	
	Tridentata karboxylerade diaminer, t ex kapryloamfodipropionat	Förbjudet	
	Hexadentata karboxylerade aminer, t ex etylendiamintetraacetat	Förbjudet	
	Tetra-, pentadentata karboxylerade aminer, t ex nitrilotriacetat, iminodisuccinat	Förbjudet	
	Bi-, tridentata karboxylerade aminer, t ex glutamat, kapryliminodipropionat	Förbjudet	
	Bränsleextraktionsvätskor, t ex tri-butylfosfat	Förbjudet	
	Dikarboxylater, t ex oxalat	10 ⁻² M	
	Trikarboxylater, t ex citrat	10 ^{–3} M	



Todays requirements- part 2(2)

		Polynaftalensulfonater (PNS)	8,1 kg ren PNS per m ³ betong
	Super- plasticerare	Polymelaminsulfonater (PMS)	8,1 kg ren PMS per m ³ betong
		Polykarboxylatetrar (PCE)	1,0 kg ren PCE per m ³ betong
			0.04 log reg D\/044 g eg m ³
			betong
		Diaminer från nedbrytning av polyamider, t ex Nylon	10 ⁻¹ M
		Dikarboxylater från nedbrytning av kondensationspolymerer, t ex polyetentereftalat (PET)	10 ^{−2} M
	Plast, gummi	Polyakrylnitril (PAN)	Obegränsat. Mängd redovisas med separat materialkod enligt [5].
		Andra additionspolymerer, t ex polyeten, polypropen, nitril- och butylgummi, fullt härdad epoxi	Obegränsat
		Triaminer_t ex tris-2.4.6-dimetvlaminometvlfenol	10 ⁻³ M
	Aminer i t ex	Tetradentata aminer, t ex trietyltetramin; fri härdare	10 ⁻⁵ M ^d
	färg	Tetradentata aminer, t ex trietyltetramin; amidbundna till karboxylat	10 ^{−7} M



Comments on the requirements

- The requirements require substantial chemistry knowledge to understand
- The unit M (Molar, moles/L) needs to be translated to kg/package to be applicable in practice
- The chemistry department needs to be involved
- New area also for the chemistry department, a lot of new things to learn



Polymers with restrictions from a radwaste point of view

In case of material in objects that can be contaminated in such a way that it can't be decontaminated.

- Cellulose and other polymers containing functionalities similar to glucose
- Polyamide (including Nylon 6 and Nylon 6,6)
- Polyester (including PET)
- Polyurethane
- Polycarbonate
- Polycarboxylic acids (except polyacrylate and PMMA)
- Other condensation polymers need to be evaluated from case to case
- Polyacrylnitrile (PAN) can be used unlimited, but amounts need to be reported



Some polymers that can be used without restrictions from a radwaste point of view (due to complexing agents)

- Polypropylene (PP)
- Polystyrene (PS)
- Polyethylene (PE)
- Polyetheretherketone (PEEK)
- Fully cured epoxy
- Polytetraflourethylene (PTFE)
 - but normally not recommended from a process point of view due to fluoride
- Polyvinylchloride (PVC)
 - but normally not recommended from a process point of view due to chloride
- Polyacrylates (including PMMA)
- Most rubbers

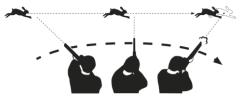


Inventory – which polymeric materials are most common in solid rad waste?

- Garbage: gloves, one time use overalls, plastic covers, tubes, wipes
- Filter aids (eg. bags to vacuum cleaners for pool cleaning)
- Paints
- Parts of components (sealings etc.) that becomes so radioactive that they can't be decontaminated



Challenges

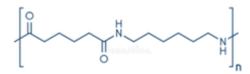


- The acceptance criteria have been changed often during recent years
 - What to do with the waste allready created?
 - The waste is active separation at source is often not feasible (ALARA)
- Full tracability of active waste is needed from purchase to radwaste
- Some polymeric materials are needed for the operation of the plants
 - e.g. cleaning wipes hard to find free from complexing agents
- Sometimes hard to get all information needed about the materials, eg. Nylon 6 or Nylon 6,6?





Pitfalls, eg. Nylon 6,6



			nylon 66
Super- plasticerare	Polynaftalensulfonater (PNS)	8,1 kg ren PNS per m ³ betong	,
	Polymelaminsulfonater (PMS)	8,1 kg ren PMS per m ³ betong	First, natural choice, but
	Polykarboxylatetrar (PCE)	1,0 kg ren PCE per m ³ betong	
	Polyvinylmaleinsyror (PVMA)	0,34 kg ren PVMA per m ³ betong	
	Diaminer från nedbrytning av polyamider, t ex Nylon	10 ⁻¹ M	
Plast, gummi	Dikarboxylater från nedbrytning av kondensationspolymerer, t ex polyetentereftalat (PET)	10 ⁻² M	
	Polyakrylnitril (PAN)	Obegränsat. Mängd redovisas med separat materialkod enligt [5].	Nylon 6,6 also generates
	Andra additionspolymerer, t ex polyeten, polypropen, nitril- och butylgummi, fullt härdad epoxi	Obegränsat	dikarboxylates, so this
Aminer i t ex färg	Triaminer, t ex tris-2,4,6-dimetylaminometylfenol	10 ⁻³ M	
	Tetradentata aminer, t ex trietyltetramin; fri härdare	10 ⁻⁵ M ^d	reguirement is
	Tetradentata aminer, t ex trietyltetramin; amidbundna till karboxylat	10 ⁻⁷ M	governing



Pitfalls, eg. Nylon 6



Tabell 3-1. Gränsvärden för koncentrationer av lösta komplexbildare, och mängder av material som kan brytas ner till komplexbildare.

Ämne/Ämnesklass Material Övre gränsvärde^a Cellulosa Isosackarinat (ISA) 10-4 Mb,c Förbjudet Oktadentata karboxylerade triaminer, t ex dietylentriaminpentaacetat α-hydroxikarboxylater, t ex glukonat Förbjudet Tridentata karboxylerade diaminer, t ex kapryloamfodipropionat Förbiudet Hygien, tvätt, rengöring, Hexadentata karboxylerade aminer, t ex etylendiamintetraacetat Förbjudet dekont. Tetra-, pentadentata karboxylerade aminer, t ex nitrilotriacetat, Förbiudet iminodisuccinat Bi-, tridentata karboxylerade aminer, t ex glutamat, Förbjudet kapryliminodipropionat Bränsleextraktionsvätskor, t ex tri-butylfosfat Förbjudet 10⁻² M Dikarboxylater, t ex oxalat 10⁻³ M Trikarboxylater, t ex citrat

VATTENFAL

nylon 6

The structure and degradation of Nylon 6 means that it must be considerd as bidentate carboxylated amine => Forbidden

Recent work at FKA

PolyakryInitril		PAN	Mängd behöver redovisas med unik materialkod, kan dock användas obegränsat.	
Polyamid	Nylon Nylon 6,6	PA	Kan ge både dikarboxylater och diaminer som nedbrytningsprodukt, vilka har begränsningar. Undantag PA6, PA11 och PA12 se nedan.	
	Nylon 6	PA6	PA6 skulle kunna tänkas binda bidentat och behöver utifrån nuvarande kravbild betraktas som totalförbjuden.	
	Nylon 11 Nylon 12	PA11, PA12	Är för långa för att kunna bilda komplex. Kan användas obegränsat.	
Polyester		PES	Kan ge dikarboxylat som nedbrytningsprodukt och har således begränsningar om det inte kan visas att aktuell polyester inte ger dikarboxylat som nedbrytningsprodukt.	
Polyetereterketon		PEEK		
Polyetentereftalat		PET	Är en polyester och kan ge dikarboxylat som nedbytningsprodukt. Begränsningar råder.	
Polyeten		PE, LDPE HDPE		

- List of polymeric materials- colour coded from a rad waste point of view.
- Makes it easier for engineering department to make good choices for materials that risk getting high enough contamination that it needs to be sent to SFR



Recommendation

- Ask chemistry department at your plant for help with evaluation
- In case of uncertainties, contact SKB for guidance

