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



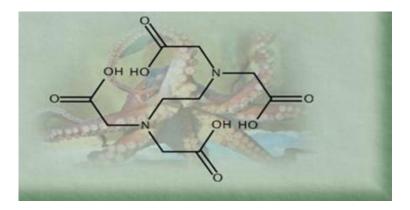
What is a complexing agent?

- 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.

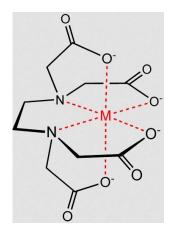


What is a complexing agent?

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

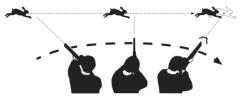


Inventory – which polymeric materials are most common in solid rad waste?

- 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

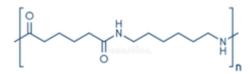


- The acceptance criteria have been changed often during recent years
 - What to do with the waste allready created?
 - The waste is active separation at source is often not feasible (ALARA)
- Full tracability of active waste is needed from purchase to radwaste
- Some polymeric materials are needed for 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?





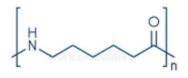
Pitfalls, eg. Nylon 6,6



| | | | 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

