Theia workshop 2018

Techniques and Issues in Gd Water Doping

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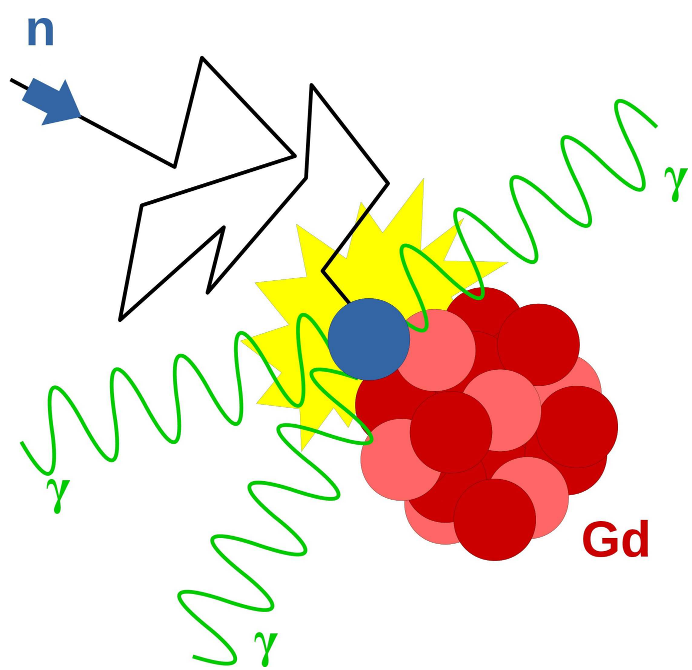
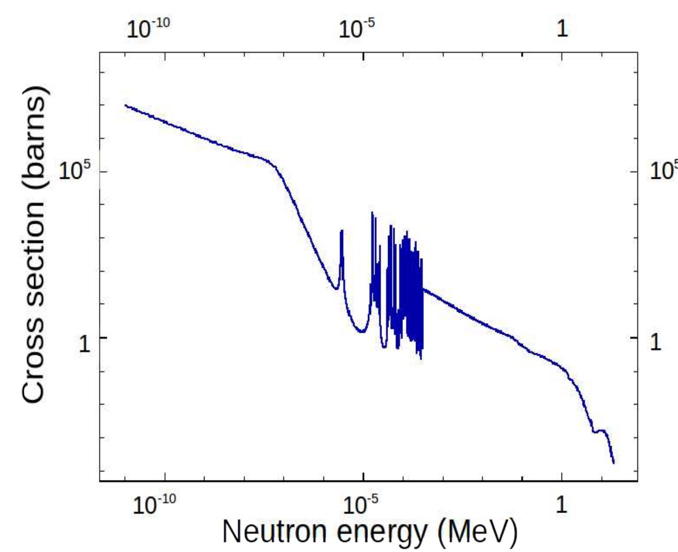
Why load water with gadolinium?

Gadolinium greatly increases the neutron detection efficiency

- Gadolinium (Gd) has a **very high neutron capture cross section** (49,000 barns)
- **~8 MeV of energy** → More light to detect and above most random radioactivity



- Gadolinium-loaded water has been used in **Watchboy** and **EGADS**
- Requires a soluble compound of gadolinium: **Gd chloride** ($GdCl_3$) or **Gd sulfate** ($Gd_2(SO_4)_3$)
- Low cost: ~$50 per kg (small quantities)



ENDF neutron capture cross section on Gd157

How to load water with gadolinium?

- Gd chloride and sulfate are **highly soluble**
- **One concern**: Gd hydroxide (GdOH) isn't

  → Care must be taken to keep Gd-loaded water acidic (pH < 7)
- Both compounds show similar characteristics

Gadolinium chloride

Gd chloride ($GdCl_3$)

- Pros:
  - High transparency
  - No UV absorption
  - High solubility → Up to 50% by weight
  - Better tolerance to bacterial growth
- Cons:
  - Lower material compatibility

Gd sulfate ($Gd_2(SO_4)_3$)

- Pros:
  - High transparency
  - No UV absorption
  - Better material compatibility
- Cons:
  - Lower solubility → Up to 2% by weight
  - Some bacteria eat sulfur

Filtering pure water

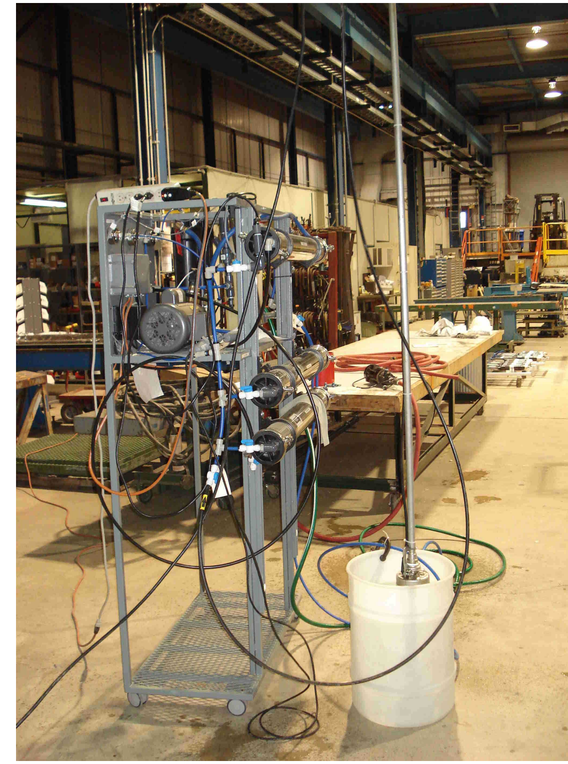
- Large water detectors **need to recirculate and purify their water** in order to keep high levels of transparency

- Cleaning of ultrapure (DI) water → Removal of all impurities but H_2O

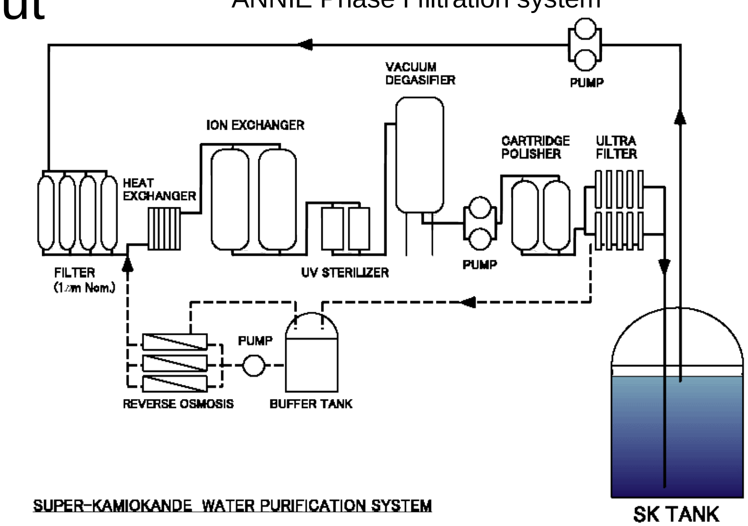
- Common parts in water filtration systems:
  - **Microfilters** - Pore size > 0.2 microns
  - **Ultraviolet lamps** - 254 nm to kill biologics
  - **De-ionizing ion exchange resins** - Remove all but H^+ and OH^- ions

- Keep impurities level low → **18 MΩ.m ~> 30 ppt**

- Although sometimes big, these filtration systems aren't "technologically challenging"



ANNIE Phase I filtration system



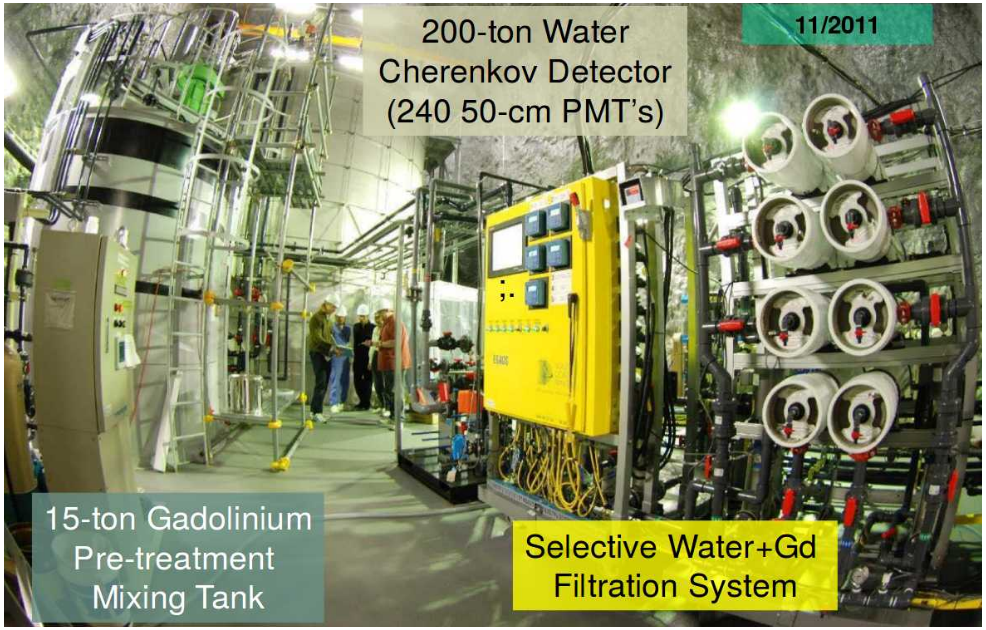
Filtering Gd-loaded water

- The goal is similar than for DI water → Remove impurities
- However, on a DI water point of view, gadolinium and sulfate ions are impurities
- The use of de-ionizing resins is prohibited as it will remove Gd
- Dedicated filtration systems have to be developed
  → See Mark Vagins' talk on SuperK-Gd

The EGADS approach:

Use a series of ultra- and nano-filters to separate 'Gd-loaded water' from 'pure water + impurities'

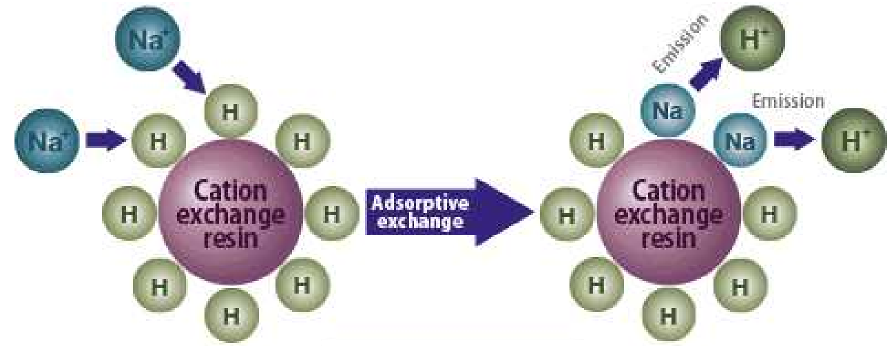
Scalable to the needs of SuperK



EGADS filtration system (from Mark Vagins)

A word on ion exchange

- Ion exchange: **Exchange of ions** between an electrolyte solution and a complex
- Ion exchangers are usually **resins** → Plastic beads (polystyrene and divinylbenzene)
- Resins have **functional groups** onto which are bound ions
- Resins exist in the anion (-) or cation (+) form:
  - **Anion** → OH^-, Cl^-, etc...
  - **Cation** → H^+, Na^+, Ca^{2+}, etc...
- Non-ionic resin exist to remove long organic chains
- Flowing $Gd_2(SO_4)_3$ through an OH^- resin would create GdOH → **Not good**!
- Flowing $Gd_2(SO_4)_3$ through an H^+ resin would create H_2SO_4 → **Not good either**!



From astom-corp.jp

Resin beads at UC Davis

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Water filtration for ANNIE

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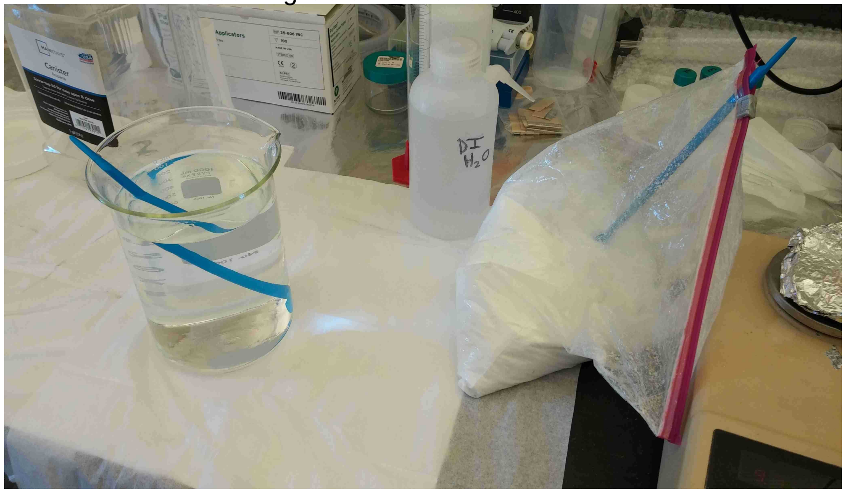
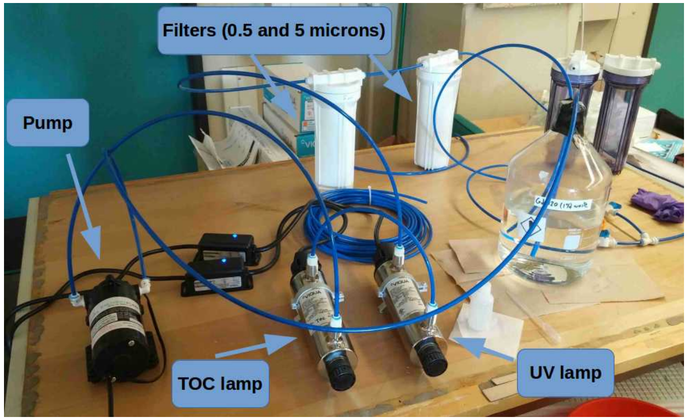
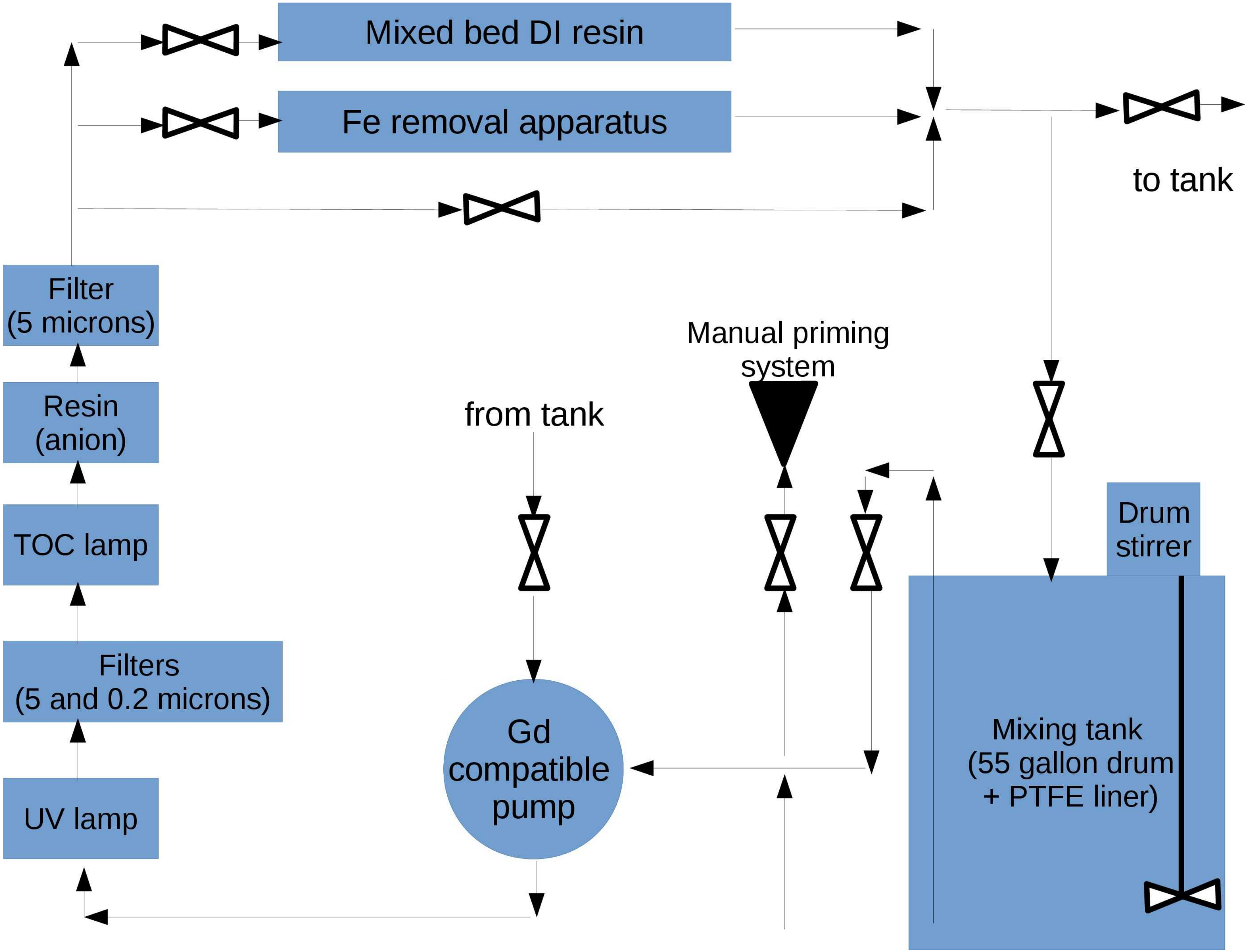
- **ANNIE Gd-loaded water → 0.2%** ($Gd_2(SO_4)_3$)
- Gd and water system R&D done at UC Davis
  - **Gd compatibility tests**
  - **Filtration system development**
- R&D **partially common with EGADS** (through Mark Vagins, an ANNIE collaborator)
- But budgets aren't the same unfortunately
- Need a **cheaper**, yet **efficient**, filtration apparatus
- Tabletop filtration system to scale up (30-ton tank)

Dissolving Gd sulfate at UC Davis





Water filtration for ANNIE



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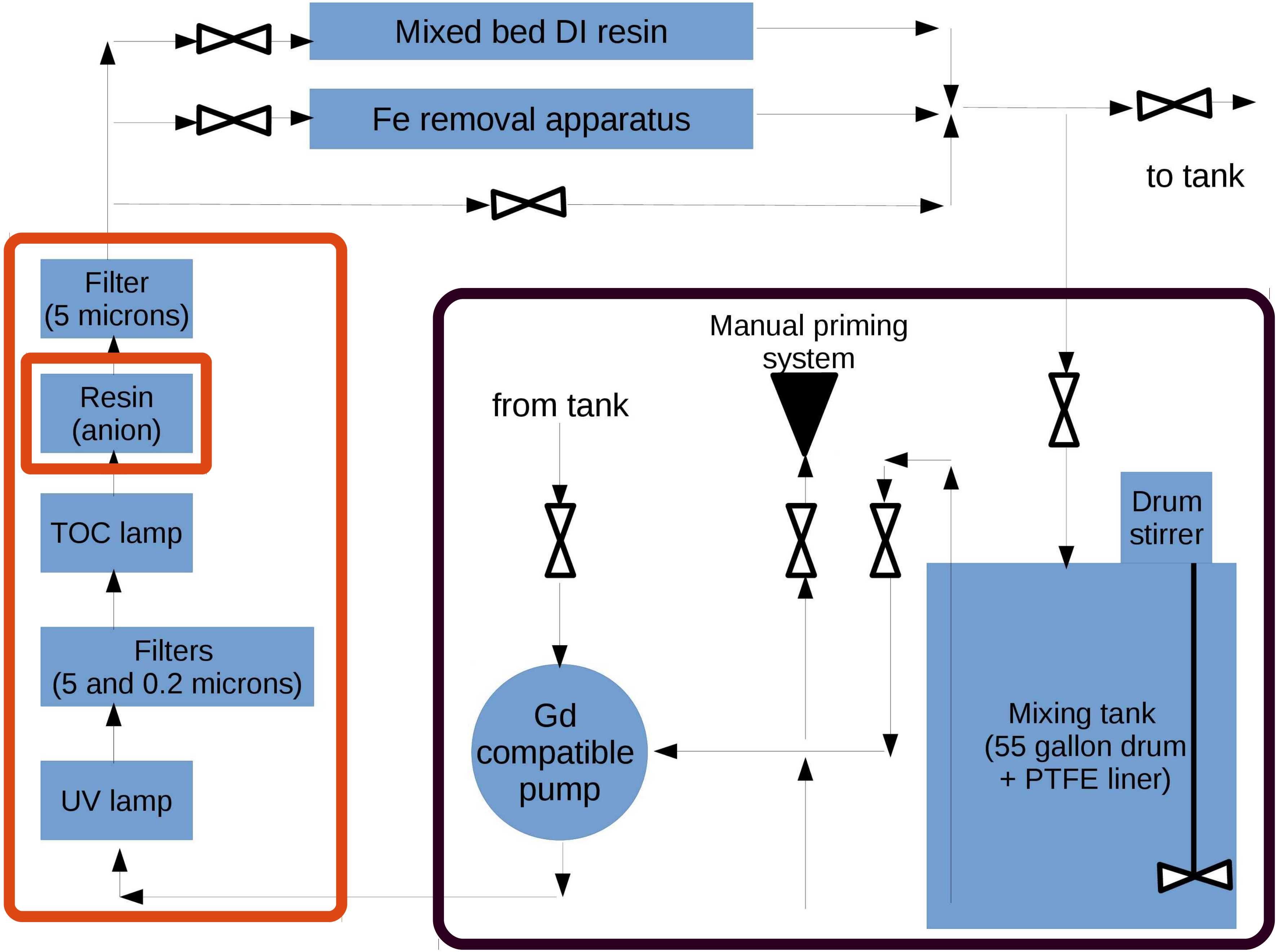
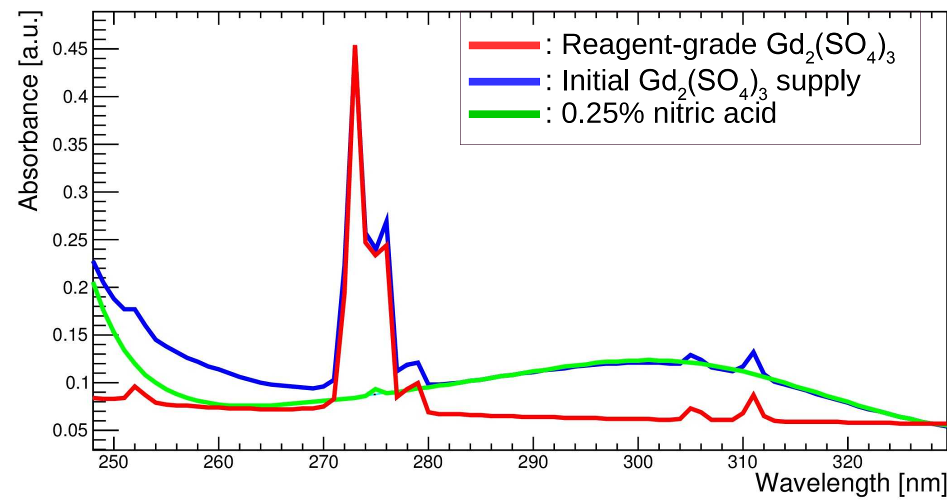
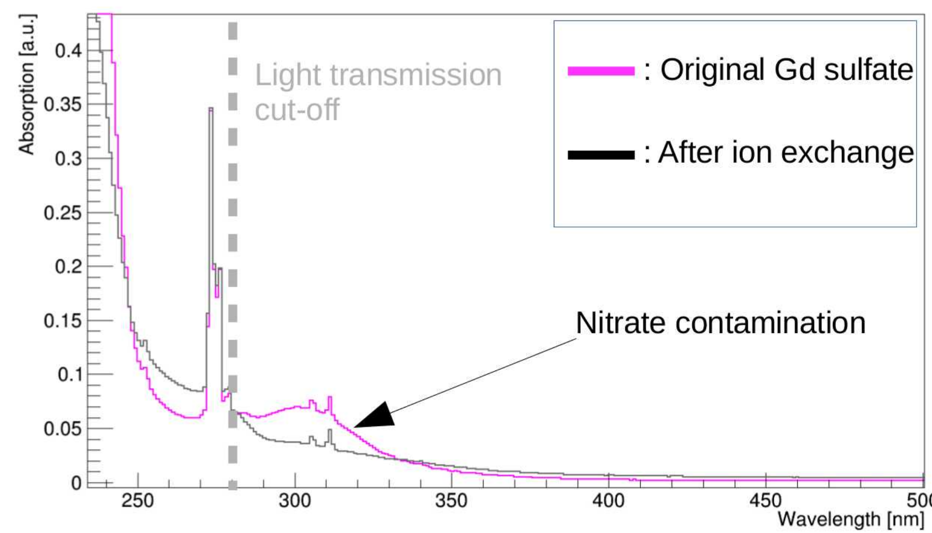


Gd filtration – Anion removal

- The original ANNIE gadolinium supply was **contaminated with nitrates**
  → Originated from the Gd extraction process
- A lot of effort was put into removing NO_3^-
- Idea → Use an **anion exchange resin**
- However, those resins come preloaded with OH^- or Cl^- ions → Creates GdOH (insoluble) or $GdCl_3$ (not wanted)
- Solution → **Exchange OH^- ions for SO_4^{2-} ions** to make the resin impervious to SO_4^{2-} and able to let $Gd_2(SO_4)_3$ pass through





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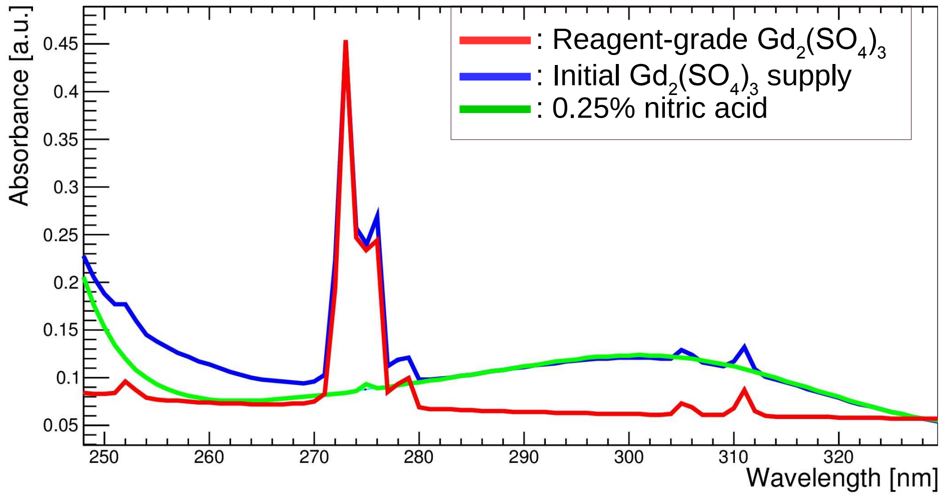
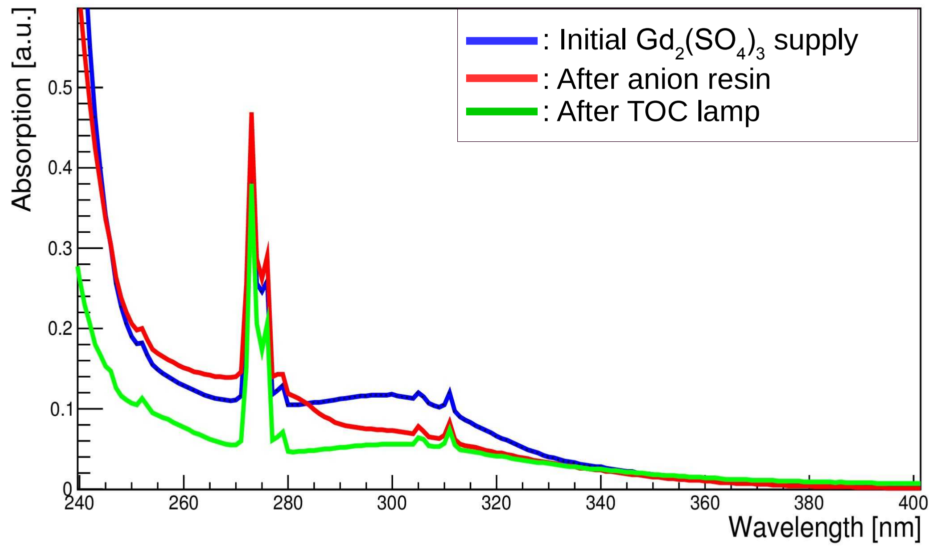
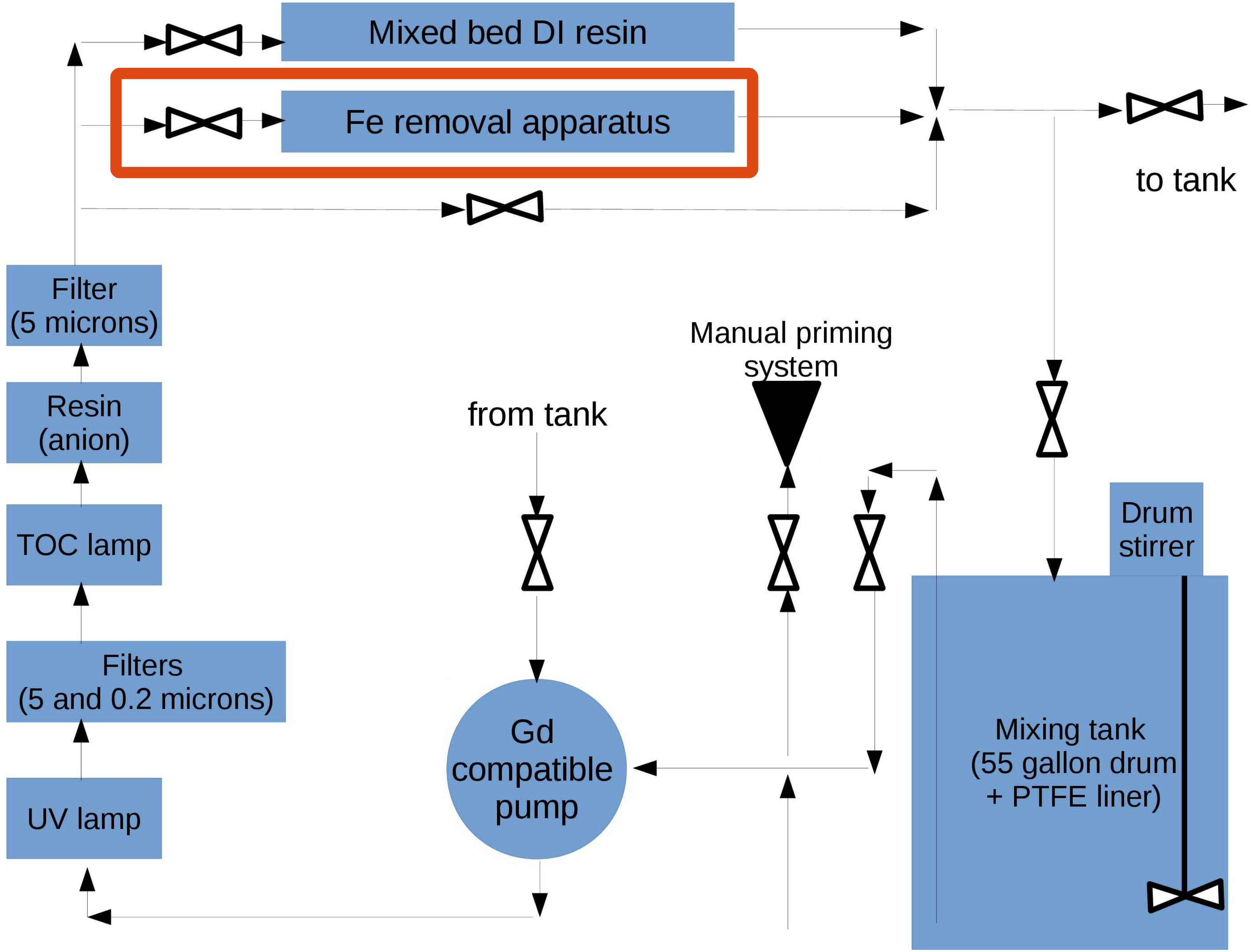
- Solution → **Exchange OH^- ions for SO_4^{2-} ions** to make the resin impervious to SO_4^{2-} and able to let $Gd_2(SO_4)_3$ pass through
- Becomes fully efficient in combination with a TOC lamp (Total Organic Carbon, 185 nm)
- We obtained a **purer Gd supply** (thanks Mark!) but this tuned resin will still be used to catch other anion contaminants





Water filtration for ANNIE



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Gd filtration – Iron removal

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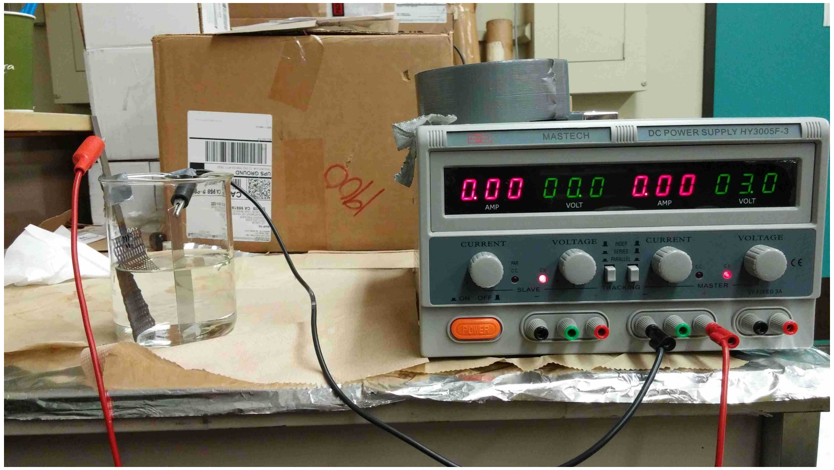
- Ppb levels of iron in water can **greatly lower UV transparency** (*W. Coleman et al., Transparency of 0.2% GdCl3 doped water in a stainless steel test environment, NIM A 595 (2008) 339–345*)
- Most detectors have a stainless steel structure
- However, **iron chemistry in water is no easy science** *(spoiler alert: it's even worse in WbLS)*
- In acidic solutions, iron tends to be fully dissolved → Harder to remove
- We are trying to use **electrolysis** to plate iron onto an electrode and remove it
- Given the pH of our solution, we assume most of the **iron in the water forms colloids** (insoluble but in suspension)
- In this case, iron could be removed using ultra- or nano-filters
- Next step → Use an **ultra-filter** to remove iron colloids from an iron-spiked Gd-loaded water solution

Electrolysis test setup



DOW IntegraFlux™ Ultrafiltration (UF) module

30 nm pore size

Gd compatibility studies

- Although less reactive than Gd chloride, Gd sulfate might still **react with some materials** more than DI water does

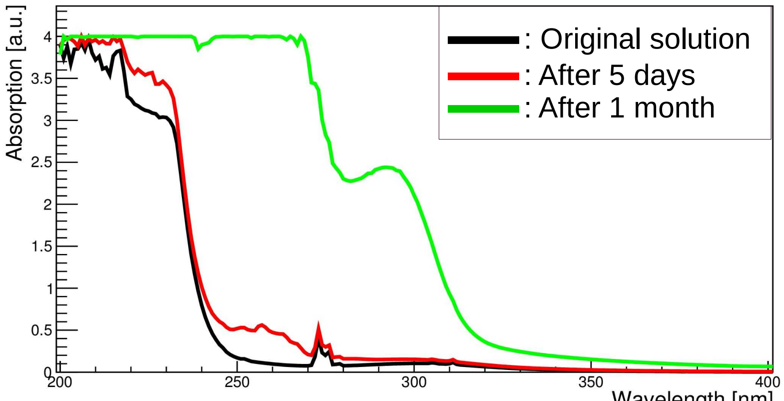
- Compatibility studies must be performed to ensure:
  - **Gd water does not degrade the material**
  - **The material does not degrade Gd water**

- Rate of degradation depends on the Gd **concentration**, the **pH** of the solution , the **temperature**, etc...

- Known problematic materials:
  → Nylon, copper, steel

- Known “safe” materials:
  → PTFE, polypropylene, acrylic, 304/316 stainless steel

After 1 month



If abs. = 0.1, att. length = 45 cm

Gd compatibility studies - ANNIE

- ANNIE Phase II: **0.2% Gd sulfate**
  → Compatibility tests done with a 1% solution for faster results

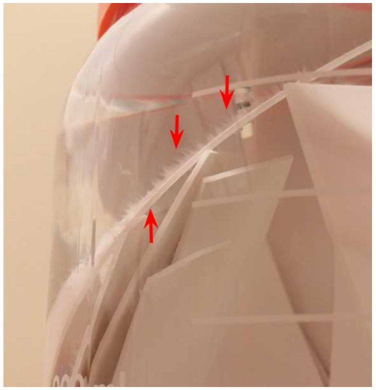
- **All tank materials are being tested**: Plastic liner, stainless steel screws, cables, etc.. and even 2 entire photomultiplier tubes

- Most materials show **no apparent degradation and no loss of water transparency**

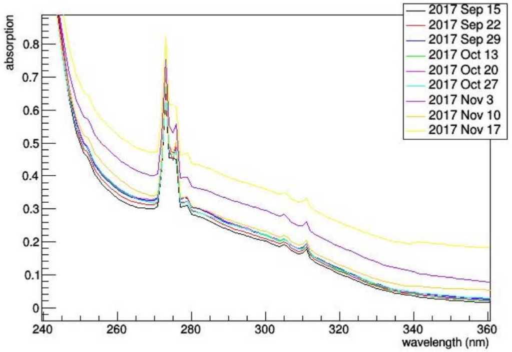
- Example of an incompatible material
  → The tank PVC liner:
  - Visible degradation
  - Increase of absorbance
  - Attenuation length much lower than the tank size
  - Possible causes: UV stabilizers in PVC, acidity of the solution

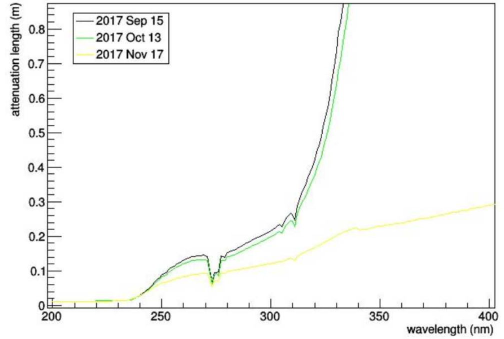
Samples for Gd compatibility tests

liner



liner





Credit: **Julie He** and **Lena Korkeila** (UC Davis)

Conclusion and take-home message

- Gd-loaded water is an **efficient** and relatively **cheap** detector medium
- With the imminent start of **SuperK-Gd** and the construction of **ANNIE** and **WATCHMAN**, a lot of R&D has been performed on loading techniques
- Dissolving gadolinium compounds in water is easy in itself but **comes with caveats**
- **Dedicated filtration systems** must be developed
- **Great care** must be taken when **deploying materials** in the water
- **Removal** of gadolinium isn't challenging but its disposal is **regulated**

THANK YOU FOR YOUR ATTENTION