KRÜGER WABAG

in Zusammen-
arbeit mit WISUTEC

EAN-NORM workshop

Dresden, 06.12.2012

Uranium in water treatment

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VEOLIA WATER

Solutions & Technologies

Drinking water treatment processes for uranium removal

Demonstration of drinking water treatment processes for uranium removal

- Adsorption at activated carbon
- Coalugation and precipitation
- Softening via precipitation
- Membrane process (NF und UO)
- Adsorption at GEH (granulated iron hydroxide)
- Ion exchange processes

Summary of the results

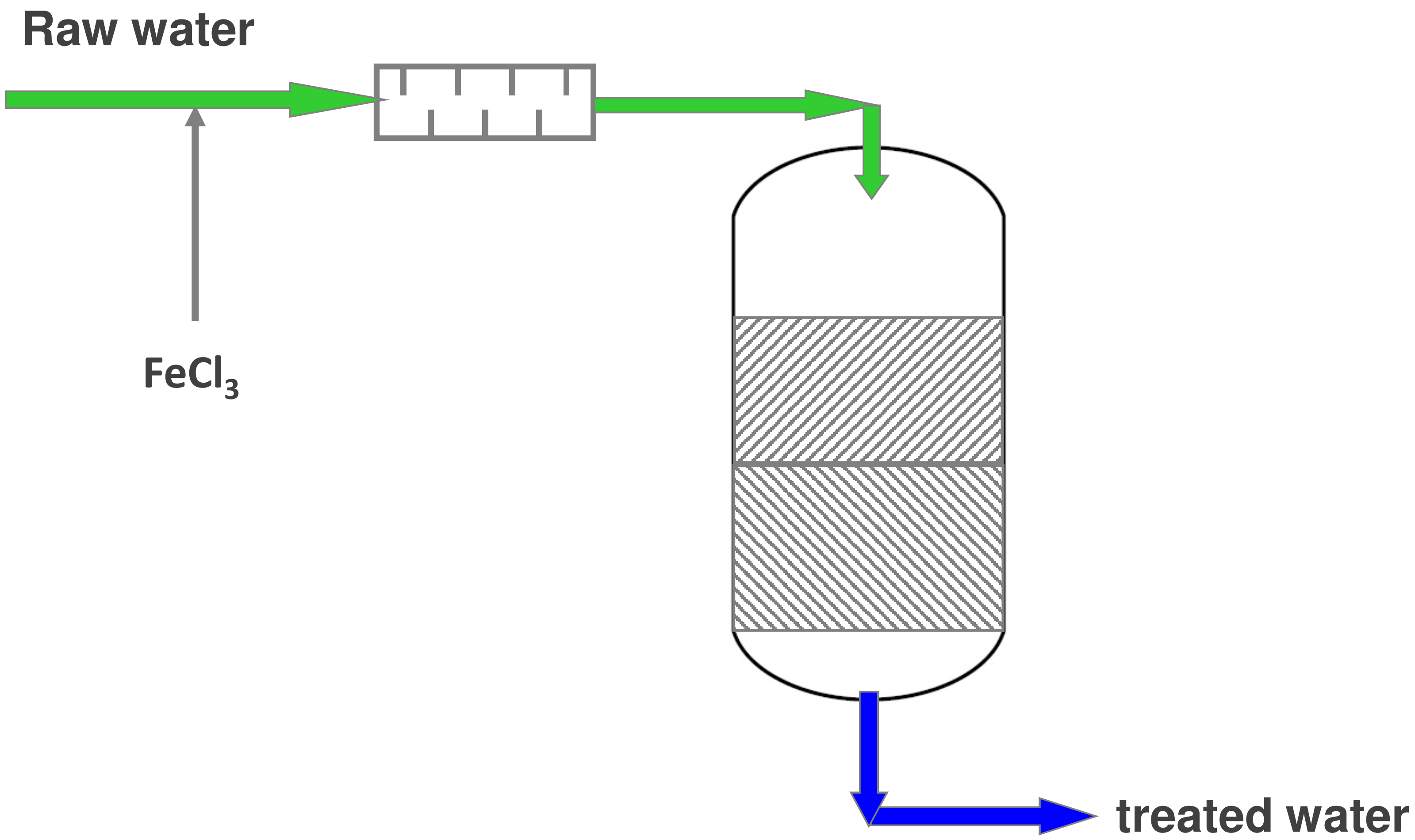
Demonstration of the suitable processes

Adsorption at activated carbon

Elimination of micro contamination, smell, taste, organic particles etc. via adsorption at activated carbon (PAK, granular activated carbon).

- η > 90 %
- low uranium concentration and up to a capacity of 5 m^3/kg
- non selective

Coagulation / Precipitation



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Coalugation / Precipitation – reaction equation

Collective precipitation of the uranium with different precipitants, that means a pollution of the sludge with uranium

- **Iron(III)chloride:**

$$FeCl_3 + 3\,H_2O \leftrightarrow Fe(OH)_3 + 3\,HCl$$

- **Aluminium sulphate:**

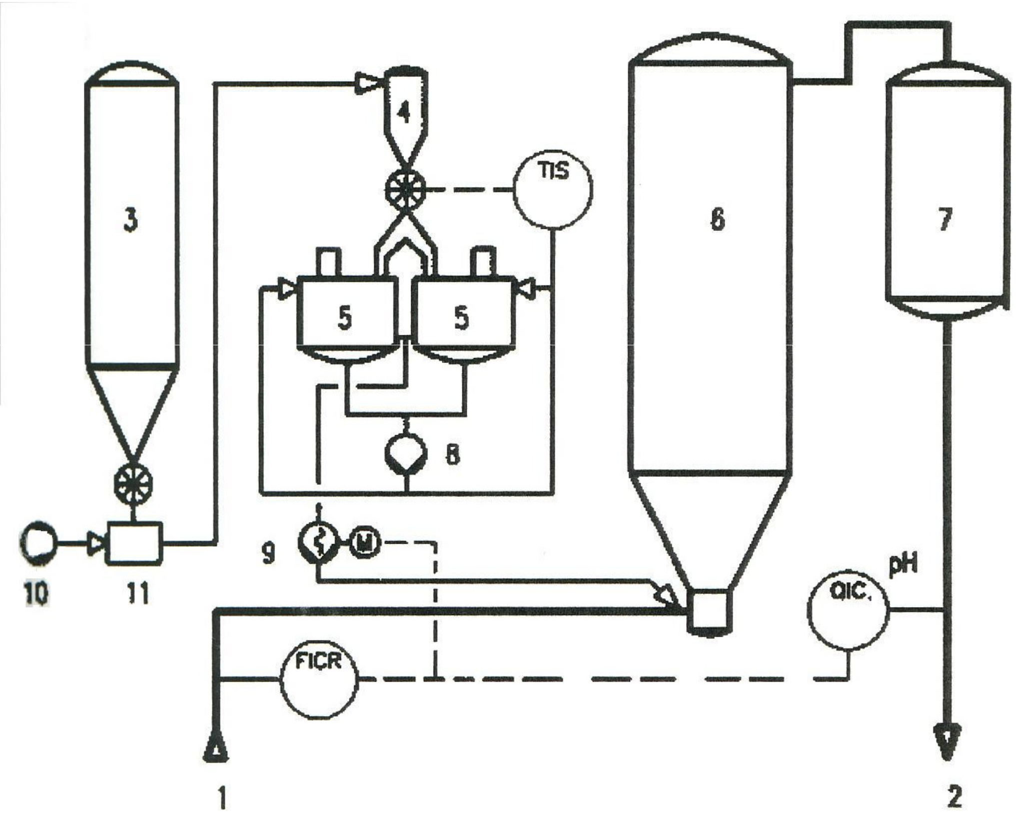
$$Al_2(SO_4)_3 + 6\,H_2O \leftrightarrow 2\,Al(OH)_3 + 3\,H_2SO_4$$

Softening via precipitation– reaction equation

Collective precipitation of the uranium with calcium hydrogen carbonate, that means a concentration of the lime sludge with uranium

- $Ca(HCO_3)_2 + Ca(OH)_2 \leftrightarrow 2\,CaCO_3 + 2\,H_2O$

Softening via precipitation



1 raw water

2 soft water

3 white lime silo

4 day silo

5 snuff-out device

6 Reactor

7 gravel filter

8 circulation pump

9 dosing pump

10 compressor

11 pneumatic conveyor

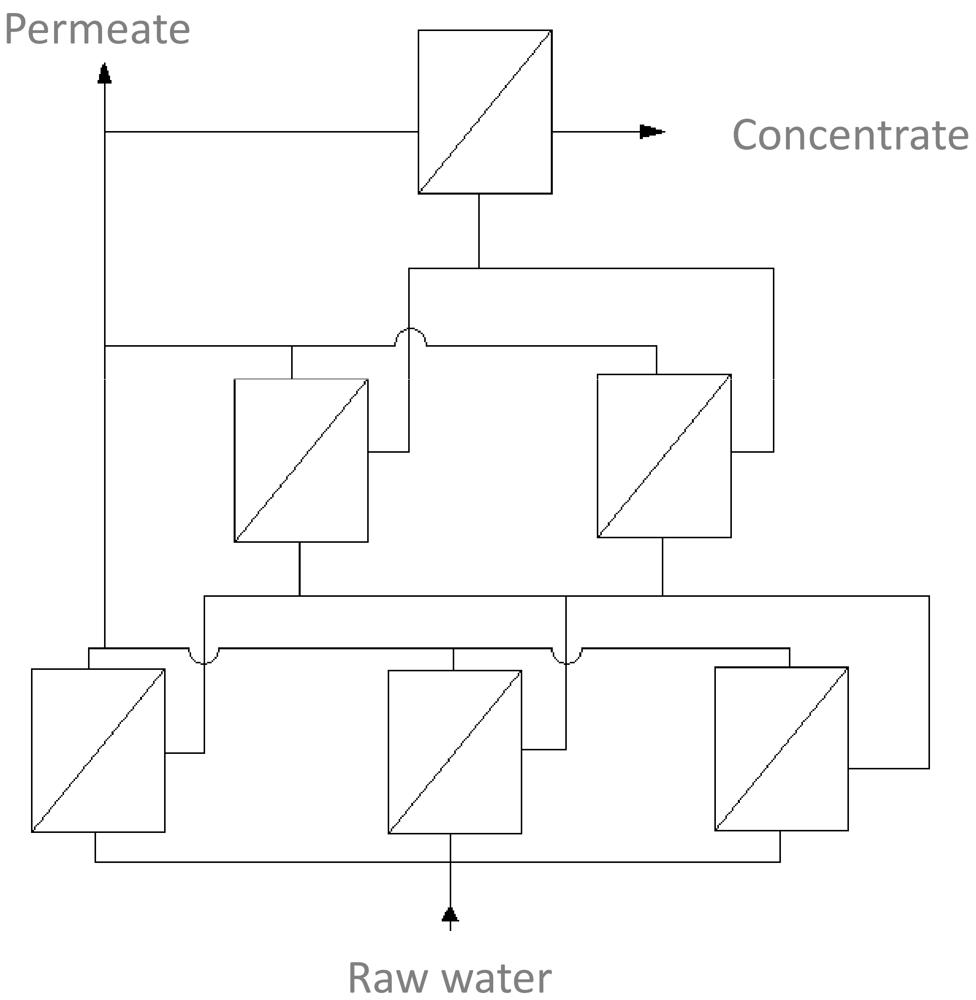
Fast decarbonisation in cylindric fast-reactor

Operation of Nano filtration/ reverse osmosis plants

- Recovery: 75 to 80 % (normally)
- Salt retention with reverse osmosis: > 98 %

- 1, 2 or 3-staged possible (fir tree controling)

Conception NF/RO plants



3. stage

2. stage

1. stage

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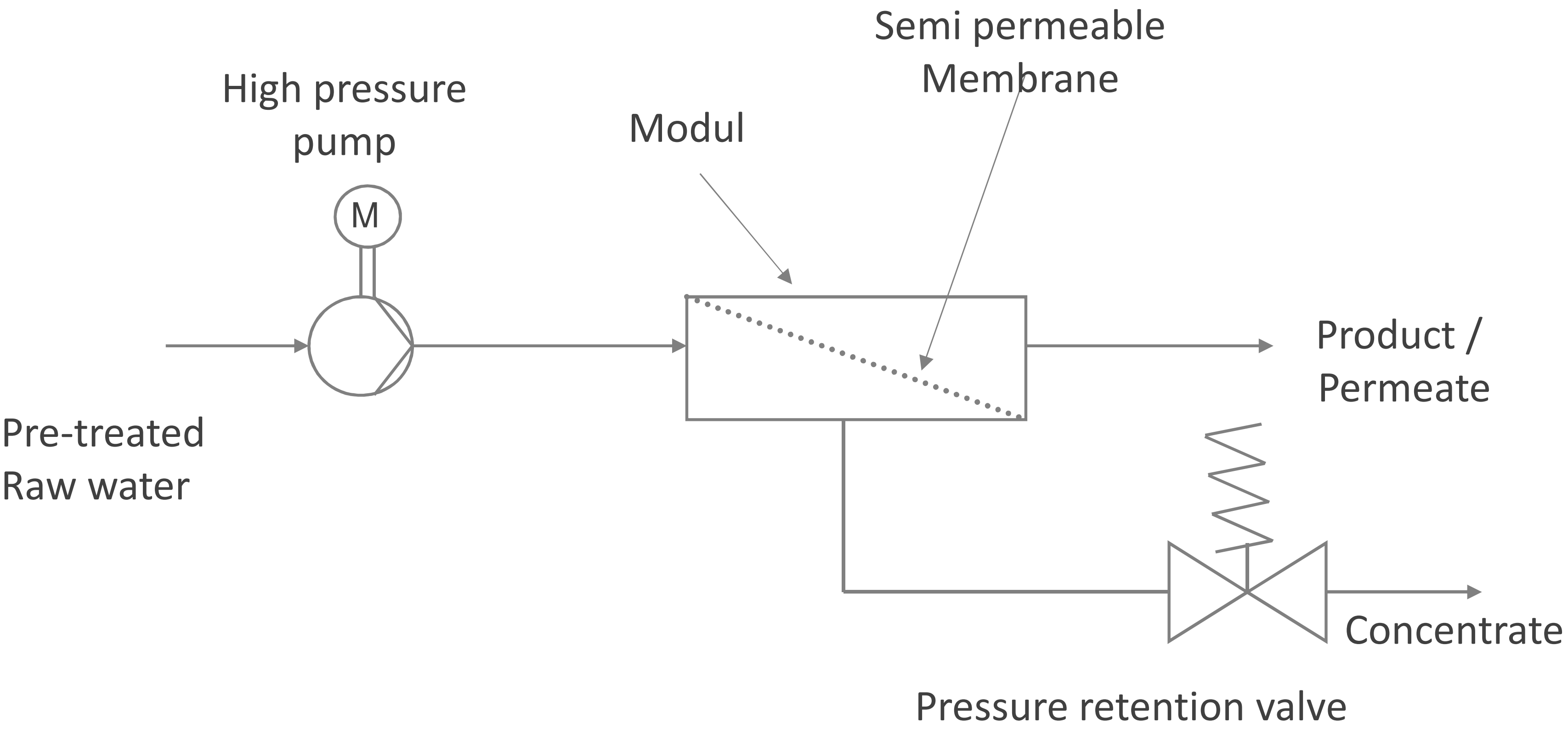
Reverse osmosis plant



basic principle of a reverse osmosis plant

Necessary treatment of reverse osmosis plants

Iron	Removal
Manganese	Removal
Aluminium	Removal
Filtratable Stoffe	Removal
Turbidity	Removal
Microbes/Germs	Reduction via desinfection or ultra filtration
Organic ingredients	E. g. adsorption at A-carbon
Barium	Anti scalant-dosage
Strontium	Anti scalant-dosage
Silicic acid	Anti scalant-dosage
Carbonate hardness	Anti scalant-dosage
Calcium sulphate	Anti scalant-dosage

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Problems for reverse osmosis plants

- Fouling (precipitation of particles)
- Scaling (crystallization of compounds)
- Biofouling (biological slime production)

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Drinking water treatment with reverse osmosis plant

- well pump station
- pre-filter(automatic flushing)
- Membrane plant – reverse osmosis for partial softening
- CO_2-Stripper
- UV desinfection
- fully automatic controlling with process control system

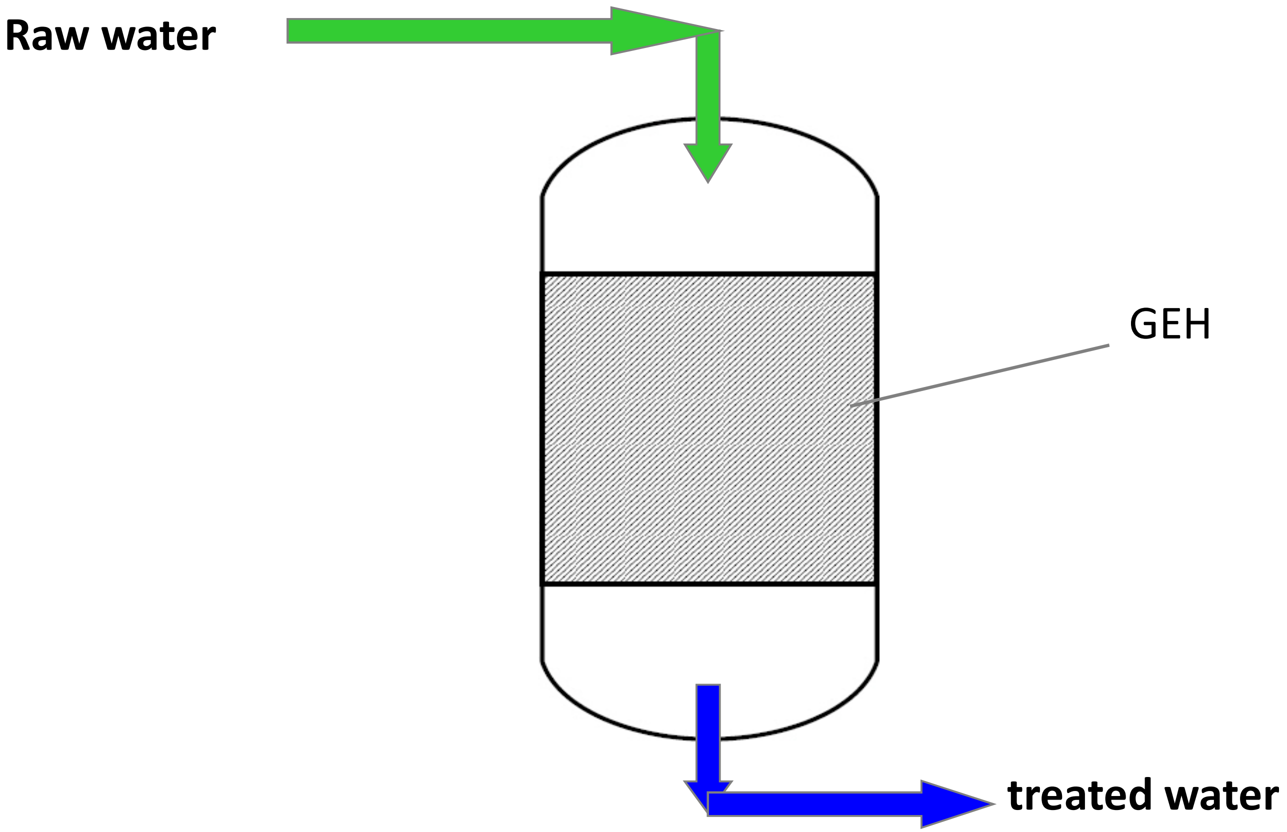
WW Osnabrück-Düstrop, 450 m^3/h, 2005

Drinking water treatment with nano filtration

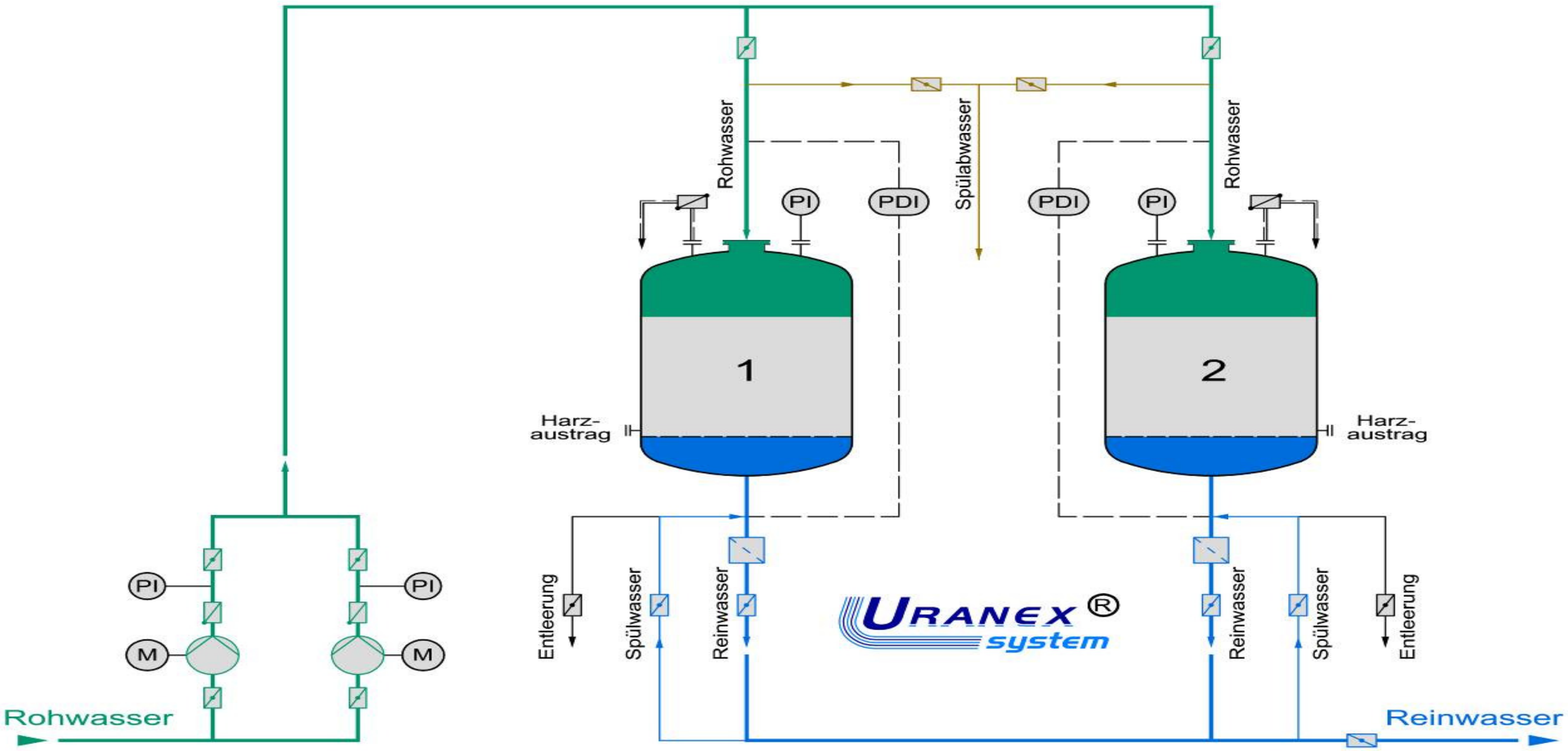
- well pump station
- pre-filter (automatic flushing)
- protective filter (filter cartridge)
- Membrane plant– Nano-filtration for partial softening
- CO_2-Stripper
- UV desinfection
- fully automatic controlling with process control system

WW Neckarbischofsheim, 100 m^3/h, 2006

Adsorption at granulated iron hydroxide (GEH)



Ion exchange - process



Ion exchange - process

Advantages

- No changes in the water composition
- Very low uranium concentration in the treated water
- Highly selective process
- easy, automated technology
- Regeneration possible

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Ion exchange - process

analytical values in Eckental:

Parameter	Unit	Raw water	treated water
Date		10.02.2005	10.02.2005
Bed volume			**40080**
conductivity/ C	µS/cm	789/9,5 C	792/9,5 C
pH		7,19/9,5 C	7,13/9,5 C
Uranium	**µg/l**	**12**	**0,07**
Nitrate	mg/l	16	16
Nitrite	mg/l	<0,01	0,01
Chloride	mg/l	84	83
Sulphate	mg/l	65	66
Phosphate	mg/l	0,05	0,05
Ammonia	mg/l	<0,4	<0,4

Ion exchange - process

References

- **2002-03** 3 pilot plants in the research centre Karlsruhe
  to test different resin types with different water matrix
- **2003-04** Pilot plant in the water work Eckental
- **2004-06** technical double plant in the water work
  Eckental due to the approval test for drinking water
  (EWP) for 2 resins.
- **2004** Beverage company in Bavaria (30 µg U/l)
- **2006** Italy, Hotel (50 µg U/l)
- **2006** Sweden, water work (145 µg/l)
- **2007** **URANEX®** -plant in Hirschaid, 1. water work
  in Germany (30 - 40 µg U/l)

Ion exchanger - process Uranex®

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Client/Location	Kind of plant	Flow capacity in m³/h	Year of construction
Beverage company in Bavaria Germany	Uranex- plant raw water 55 µg U/l	4	2004
Hotel in South Tyrol Italy	Uranex-plant raw water 50µg U/	3	2005
Water work near Oestersund Sweden	Uranex-plant Raw water 140µg U/l	6	2007
Hirschaid Community Germany	1. Uranex-plant Raw water 30µg U/l	50	2007
Maroldsweisach Community Germany	Uranex-plant Raw water 40µg U/l	35	2008
Water work Austria	Uranex-plant Raw water 120µg U/l	80	2009
Water work Austria	Uranex-plant Raw water 90 µg U/l	40	2009
Baunach City Germany	Uranex-plant Raw water 18 µg U/l	40	2010
ZV Water supply Trollmühle Windesheim, Germany	Uranex-plant Raw water 13 µg U/l	400	2011

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Ion exchanger - process Uranex®

Client/Location	Kind of plant	Flow capacity in m^3/h	Year of construction
Hirschaid Community Germany	2. Uranex-plant Raw water 28 µg U/l	28	2010
Schlüsselfeld Germany	Uranex-plant Raw water 21 µg/l	18	2011
Burgkunstadt Germany	Uranex-plant Raw water 28 µg/l	22	2011
Seßlach Community Germany	Uranex-plant Raw water $\leq$ 21 µg/l	45	2011
Bad Münster am Stein	3 Uranex-plant Raw water $\leq$ 19 µg/l	107	2012

Adsorption of uranium on a weak basic ion exchanger in comparison with GEH-Material

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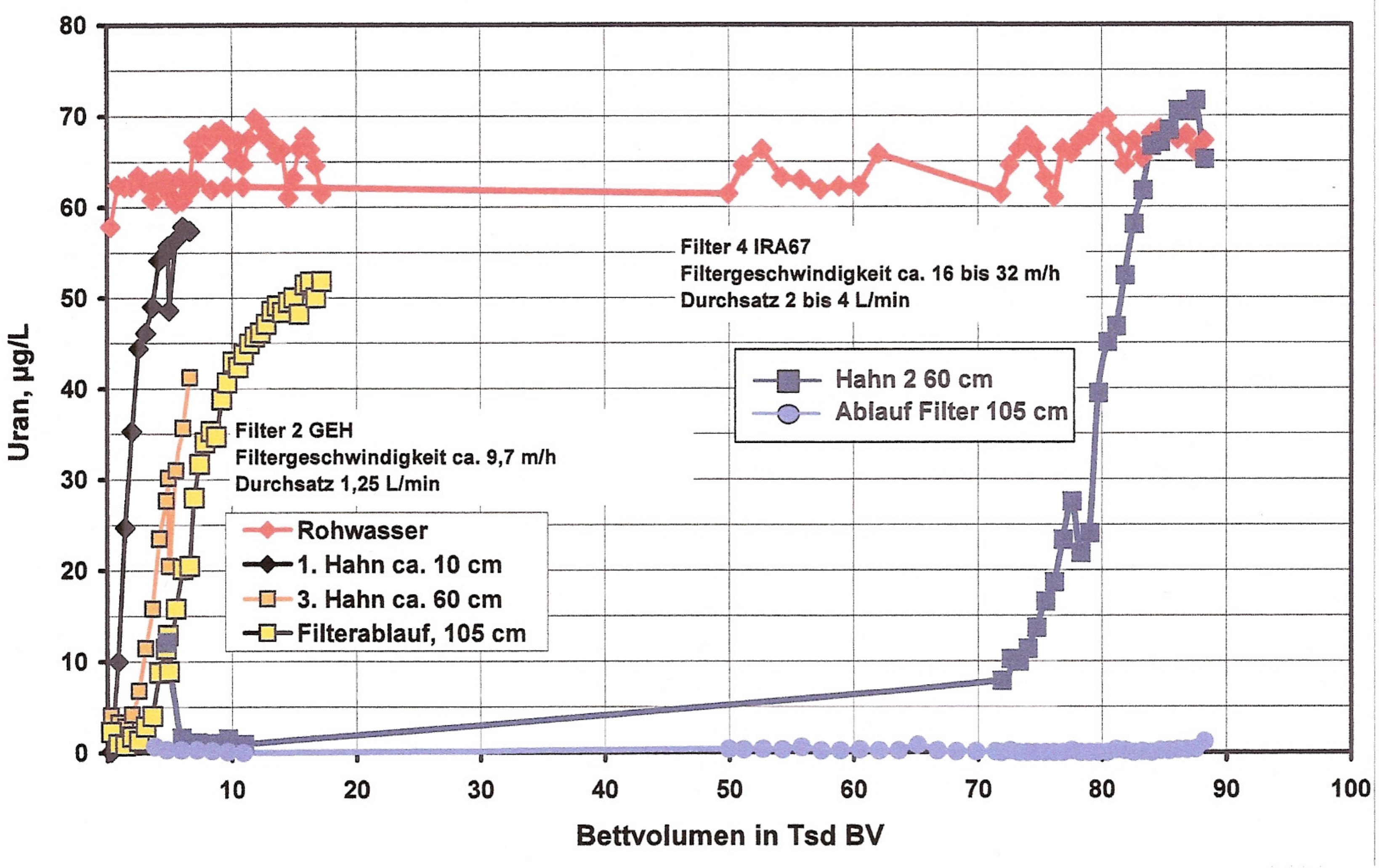

Quelle: Volker Schlitt TZW Karlsruhe, 26. Mai 2008 in Bonn

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Exchange of loaded ion exchanger via regeneration of the resins via VWS / Krüger WABAG / Wisutec according to the recycling management and waste law

Summary of the results of uranium removal

- Activated carbon filter not suitable due to short runnig time
- Oxidic sorbents are not suitable for uranium removal
- Ion exchanger are suitable for the selective uranium removal for the drinking water treatment
- Nanofiltration is also suitable for uranium removal (not selective)

Thank You for your attention!

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Ion Exchange History

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- Ion exchange processes have been proved at first in cropping soil for the element potassium.
- In 1906 the first artificial inorganic ion exchange product for water softening was launched under the product label „Permutit“.
- Organic ion exchange materials were based on natural humic acids and later on carbonic sulfonated raw material like wood, peat, lignite and anthracite coal.
- The english scientists *Adams* and *Holmes* developed in the 1930s ion exchange materials based on modified synthetic resin ion exchanger. From 1936 on these resin types were developed further by the former IG Farbenindustrie AG in Wolfen, which launched in 1938 the first synthetic ion exchange resins named „Wofatite“ (scope of application: water softening).
- In 1949 personnel of the company Rohm & Haas found out, that Uranium could be very effective absorbed by the anion exchanger Amberlite IRA 400.
- After 1955 industrial scale ion exchanger was used for hydrometallurgical production of Uranium in the USA, Canada and Australia.
- From 1965 ion exchanger are used as main technology for Uranium production in the SDAG Wismut (today WISMUT GmbH).
- Since ca. 2003 first tests were sucessfully done to use ion exchange resins for Uranium removal from drinking water (for references see KRÜGER WABAG).

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- Natural Radioactivity (NORM)
  NORM…Naturally Occurring Radioactive Materials
- Removal because of toxic effects(kidney damage), low radioactivity
- WHO guideline value 30 µg/L,
  german limit value 10 µg/L (TrinkwV from 01.11.2011)
  „suitable for the preparation of baby food“ 2 µg/L (Min/TafelWV)
- Annex 8, draft of new BSS → List of the industry sectors with NORM: „Groundwater Filtration“

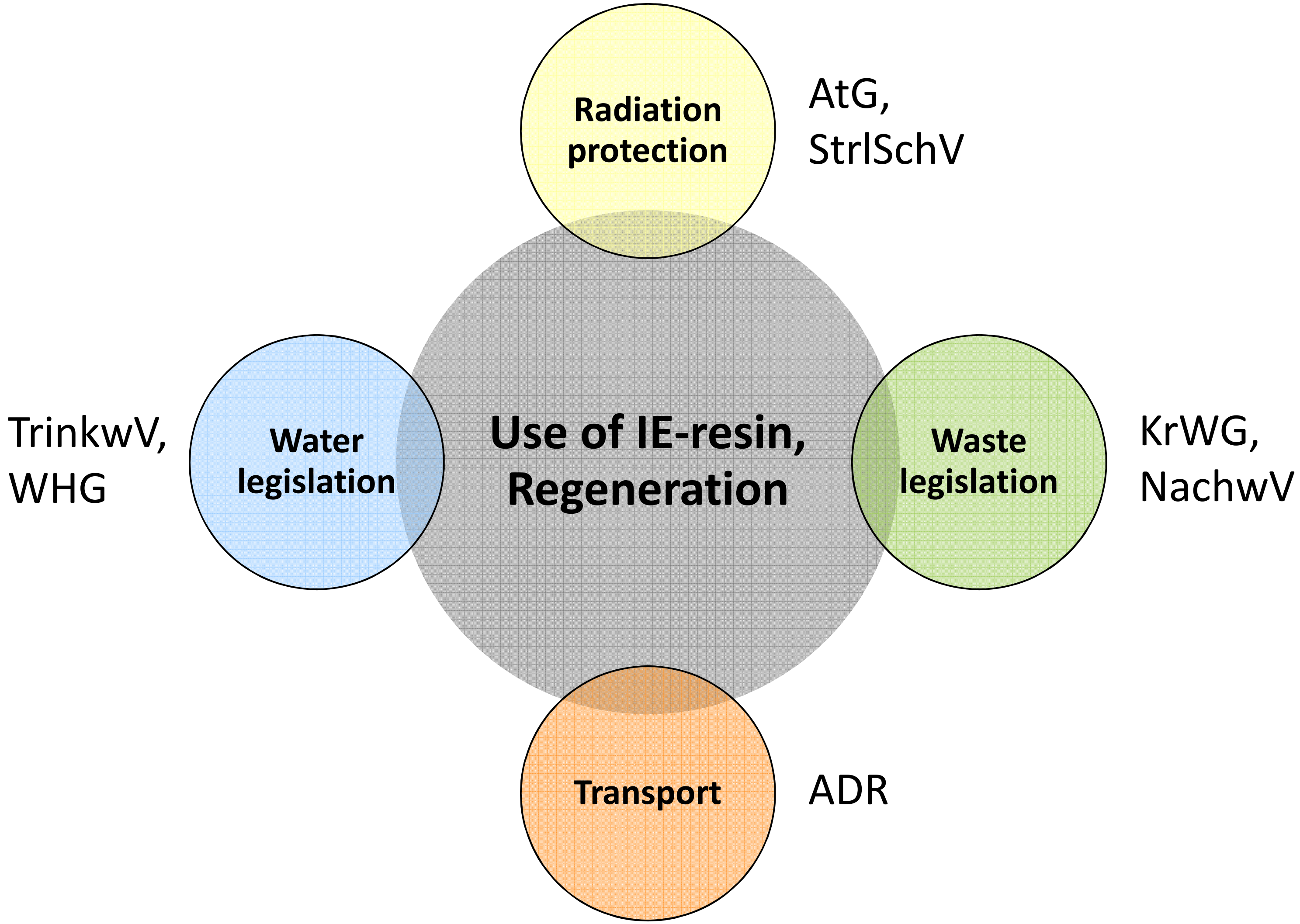
Legislation

- The Uranium removal from drinking water is done because of toxicological reasons. It has not the objective to bring the Uranium into the nuclear fuel cycle, use of Uranium is only a side-effect and closes the utilisation cycle
- Alternatively the Uranium has to be disposed of; but the disposal is not assured, that means there are problems concerning disposal company acceptance or the disposal costs are very high, so that the regeneration of the ion exchangers would become uneconomical.
- Uranium utilisation in another later process independent on the ion exchanger resins regeneration process
- Ion exchager from drinking water treatment → substance is of natural origin which is not used because of its radioactivity, as a nuclear fuel or to generate nuclear fuel (2 (2) point 3 AtG)
- Requires no surveillance according to AtG or StrlSchV
- Residues from drinking water treatment are not part of the list of residues that require surveillance according to Annex XII, part A StrlSchV
- In the explanatory statement of the StrlSchV sludges from water works are considered, but ion exchangers not. However the ion exchangers can be integrated into the basic context of the official explanatory statement of 97 StrlSchV. During handling of ion exchangers the surveillance limit values according to annex XII part B StrlSchV can be significantly exceeded. And the regeneration procedure is no so-called standard way of reutilisation or disposal.

Legislation

- At a load of between 2 g/L and 10 g/L the specific activity is between 50 Bq/g and 250 Bq/g of U-nat. Despite of the natural Uranium source the loaded ion exchager should be considered within the meaning of the legislation → classification as other materials
- **Work activities with materials** according to 3 (1) 2. StrlSchV, because the ion exchangers are produced in operational sequences (use in drinking water work) according to 3 (1) Nr. 2 b) StrlSchV and the residues resp. the ion exchangers for reutilisation according to 3 (1) Nr. 2 c) StrlSchV are incurred during recycling process.
- 102 StrlSchV as catchall element for the surveillance of other materials according to 3 Abs. 2 Nr. 20 StrlSchV, which are no residues according to annex XII part A.
- Linking of radiation protection, waste legislation and transport legislation
- Water legislation: for regeneration only materials certified for application in drinking water treatment are used (sodium hydroxide, sodium chloride, sulfuric acid and hydrochloric acid)

Legislation



Organisation

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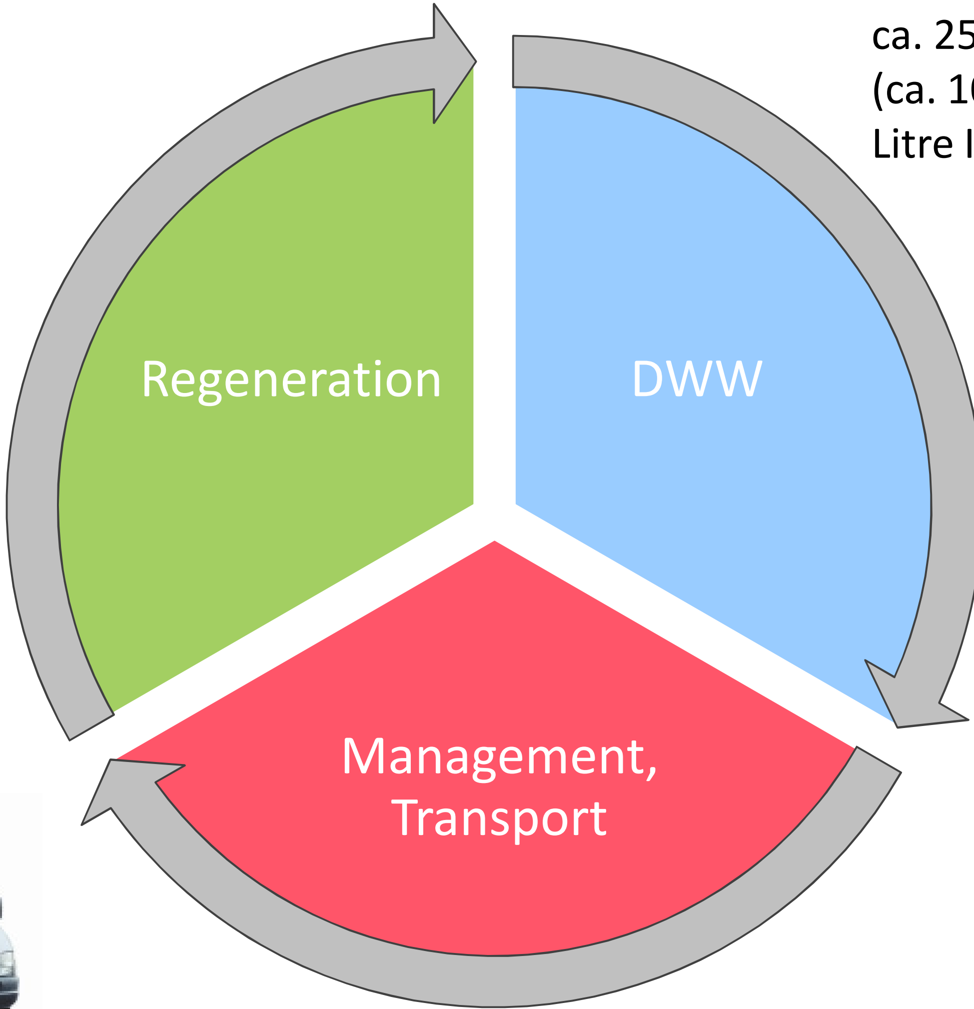
Loading IE-resin up to ca. 250 Bq/g U-nat (ca. 10 g Uranium per Litre IE-resin, Ø 4-6 g/l)



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Approval by the authorities

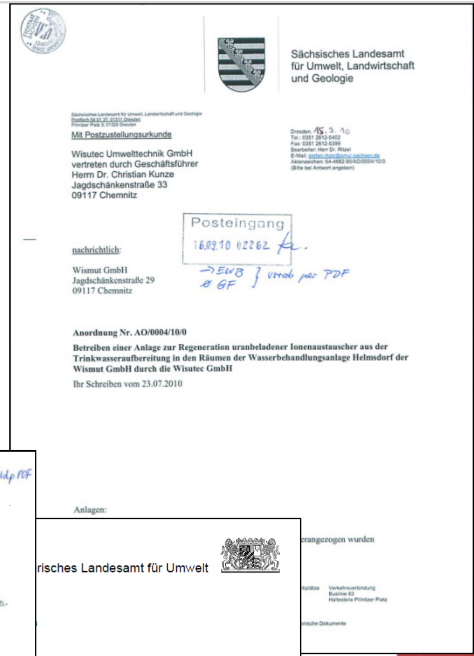
Order for operation

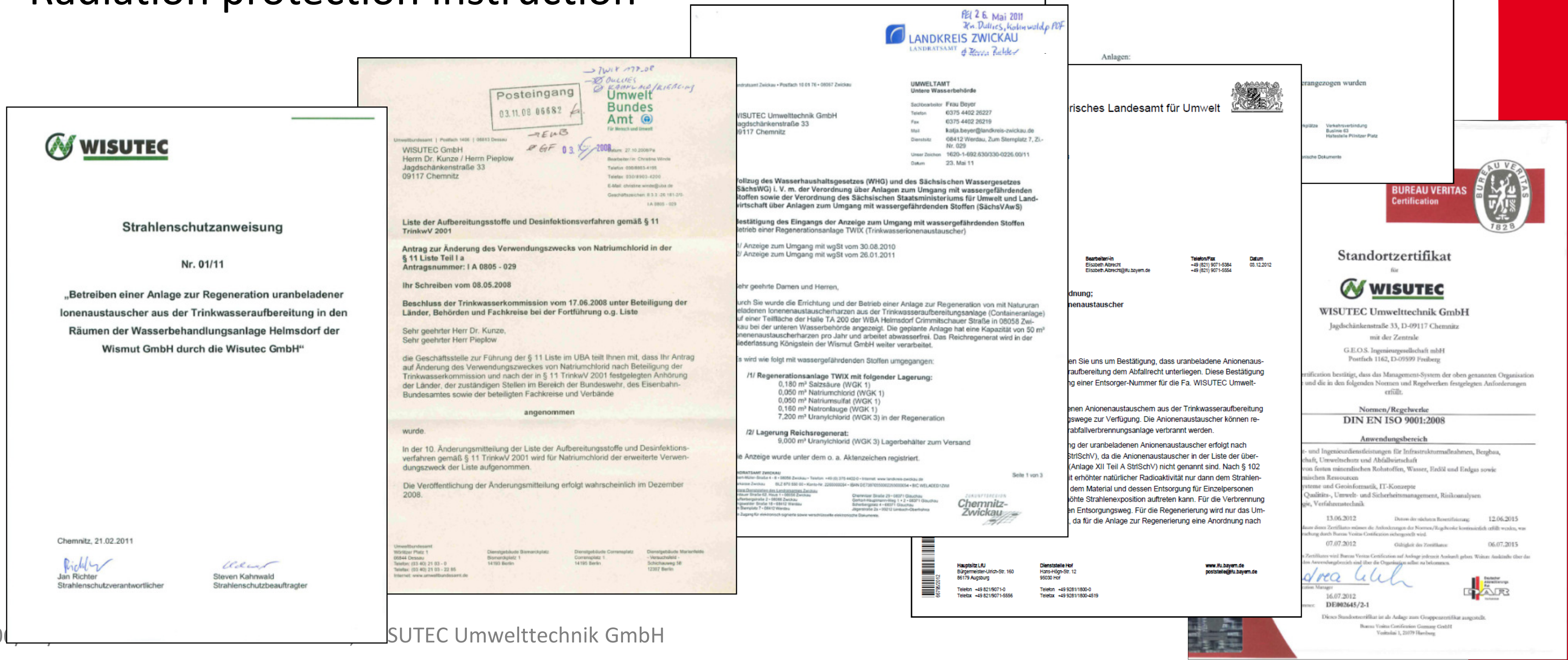
Sächsisches Landesamt
für Umwelt, Landwirtschaft
und Geologie

Anordnung Nr. AO/0004/10/0

Betreiben einer Anlage zur Regeneration uranbeladener Ionenaustauscher aus der Trinkwasseraufbereitung in den Räumen der Wasserbehandlungsanlage Helmsdorf der Wismut GmbH durch die Wisutec GmbH

- § 102 StrlSchV (surveillance of other materials)
- Radiation protection instruction





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Analyses of water before and after IE-column:

- ICP-MS : Uranium in µg/l

Analyses of IE-resin:

- Alpha and gamma spectrometry : U isotopes

→ Disequilibrium U-234 : U-238 ≈ 1.3 – 1.6 (3 examples)
→ Dry residue 30 % – 50 %

Used materials

The regeneration procedure uses the following materials (according to § 11 of the Drinking Water Ordinance parts I a and I b, list of the treatment materials and disinfection procedures):

- loaded ion exchangers of both listed types (weakly alkaline and strongly alkaline),
- Sodium chloride and hydrochloric acid for regeneration,
- Sulfuric acid or sodium hydroxide (dependent on the ion exchanger type) for equilibration and
- drinking water for flushing after regeneration.

The process of regeneration is different for both ion exchange resin types.

Plant leaving substances

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The plant leave the following substances:

- regenerated ion exchanger, equilibrated and pre-rinsed with residual amounts of sulfuric acid or sodium hydroxide (depending on type), as a measure against contamination (germination) until reuse,
- Drilling mud (average 50 kg per m^3 ion ex.) from the resin purification before regeneration (these sludges are similar to sludges from backwash of sand filters in drinking water treatment),
- Uranium bearing solution (about 2.8 m^3 solution per m^3 ion ex.) with 0.5 g/l to 3 g/l uranium,
- All internal rinse water will be used several times or substreams will be desalted by vacuum evaporation, respectively. Therefore only the regrind solution contains uranium.


TOUCH

Thank you for your attention!

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