TOWARDS A SMART & INTEGRAL TREATMENT OF NATURAL RADIOACTIVITY IN WATER PROVISION SERVICES

ALCHEMIA Preliminary Spanish results

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- Integration of the solar thermal and photovoltaic energy in buildings

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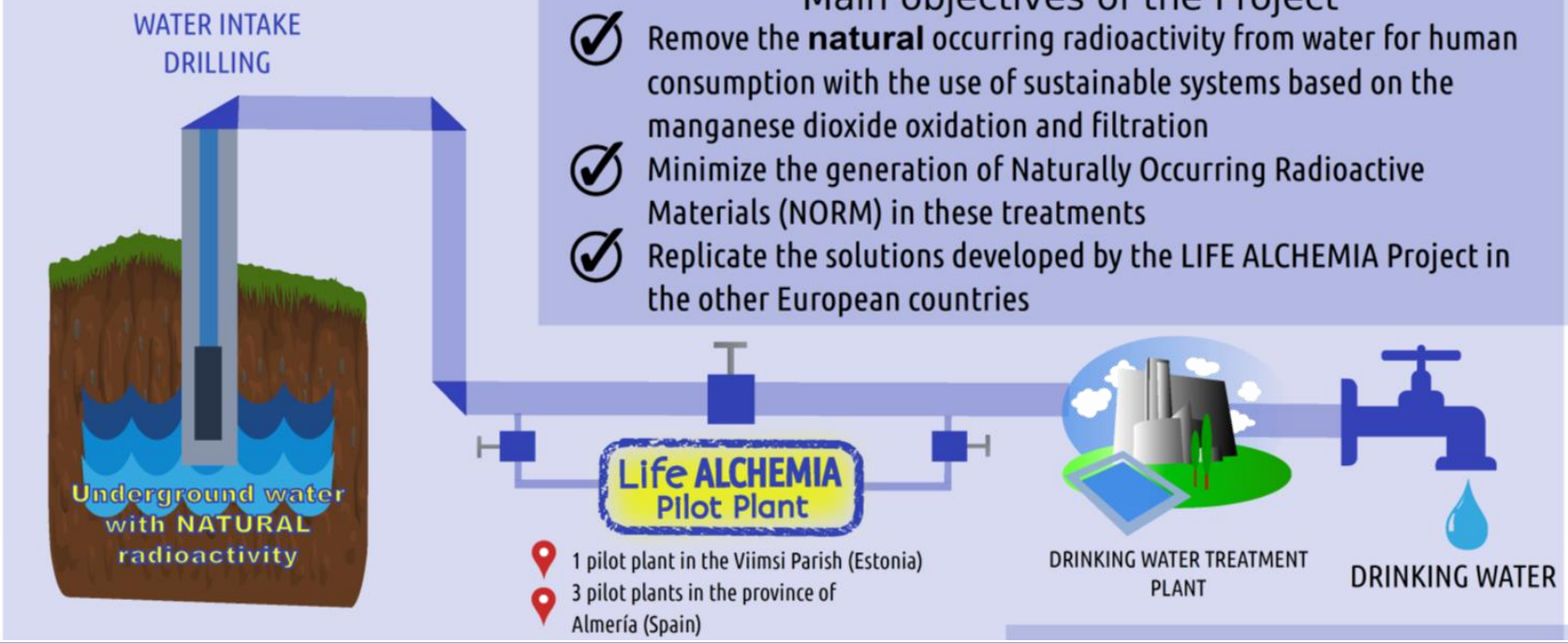
INDEX

LIFE ALCHEMIA

Towards a smart & integral treatment of natural radioactivity in water provision services

European Union programme LIFE Project (LIFE16 ENV/ES/000437)

www.lifealchemia.eu



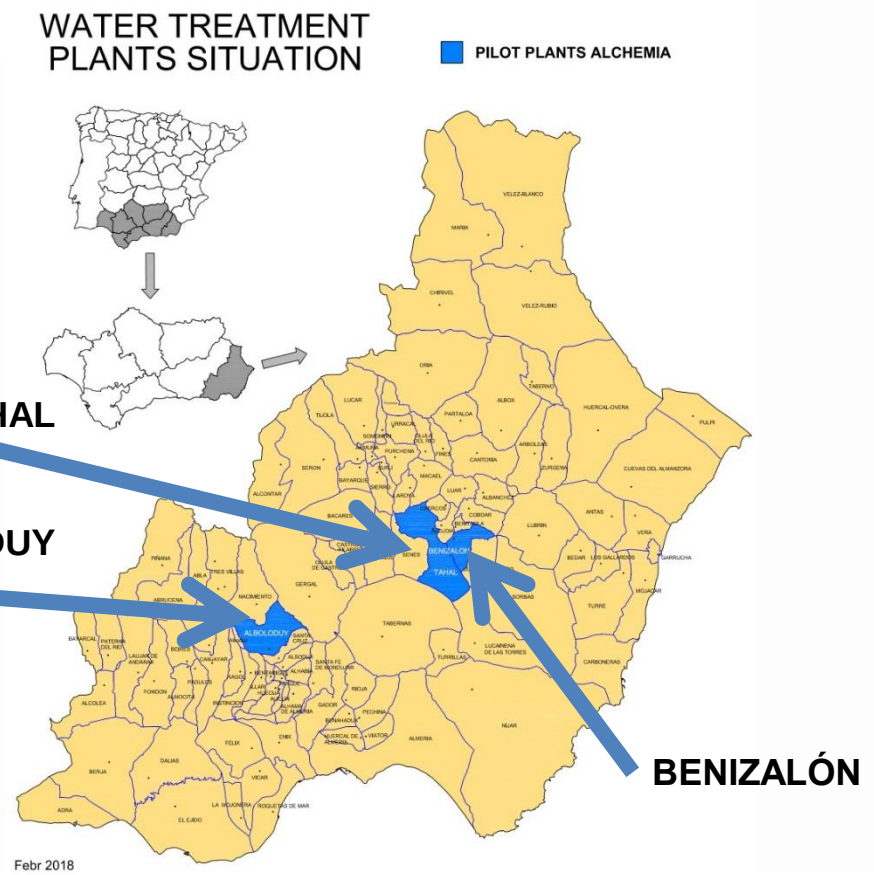
Spanish demos locations and raw water analysis

ALCHEMIA PLANTS LOCATIONS

Tahal pilot plant

Benizalon pilot plant

Alboloduy pilot plant



LABORATORIO DE RADIACTIVIDAD AMBIENTAL
UNIVERSIDAD DE EXTREMADURA
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Analytical report on radiological characterization of water from the 3 WWTPs of Alboloduy, Benizalon and Tahal

In al cases gross alpha exceed the limits and the ID were calculated

ALBOLODUY

Radionuclide	Activity (Bq/L)	% TID
^{234}U	0.218±0.031	35,46%
^{235}U	0.021±0.005	
^{238}U	0.239±0.034	35,70%
^{226}Ra	0,0035	
^{228}Ra	<0.020	
^{210}Po	<0.001	
^{210}Pb	0.008	18,32%
ID	0.0220 mSv/y	

BENIZALÓN

Radionuclide	Activity (Bq/L)	% TID
^{234}U	3.43±0.42	34,69%
^{235}U	0.090±0.013	
^{238}U	2.40±0.29	22,29%
^{226}Ra	0.195±0.017	
^{228}Ra	0.133±0.013	18,94%
^{210}Po	0.016±0.003	
^{210}Pb	0.056	
ID	0.3537 mSv/y	

Main concentrations

	U	Ra	Pb	Po
Alboloduy	74,4%	3,3%	18,3%	4,0%
Benizalón	57,9%	30,9%	8,0%	4,0%
Tahal	25,6%	59,7%	15,3%	3,1%

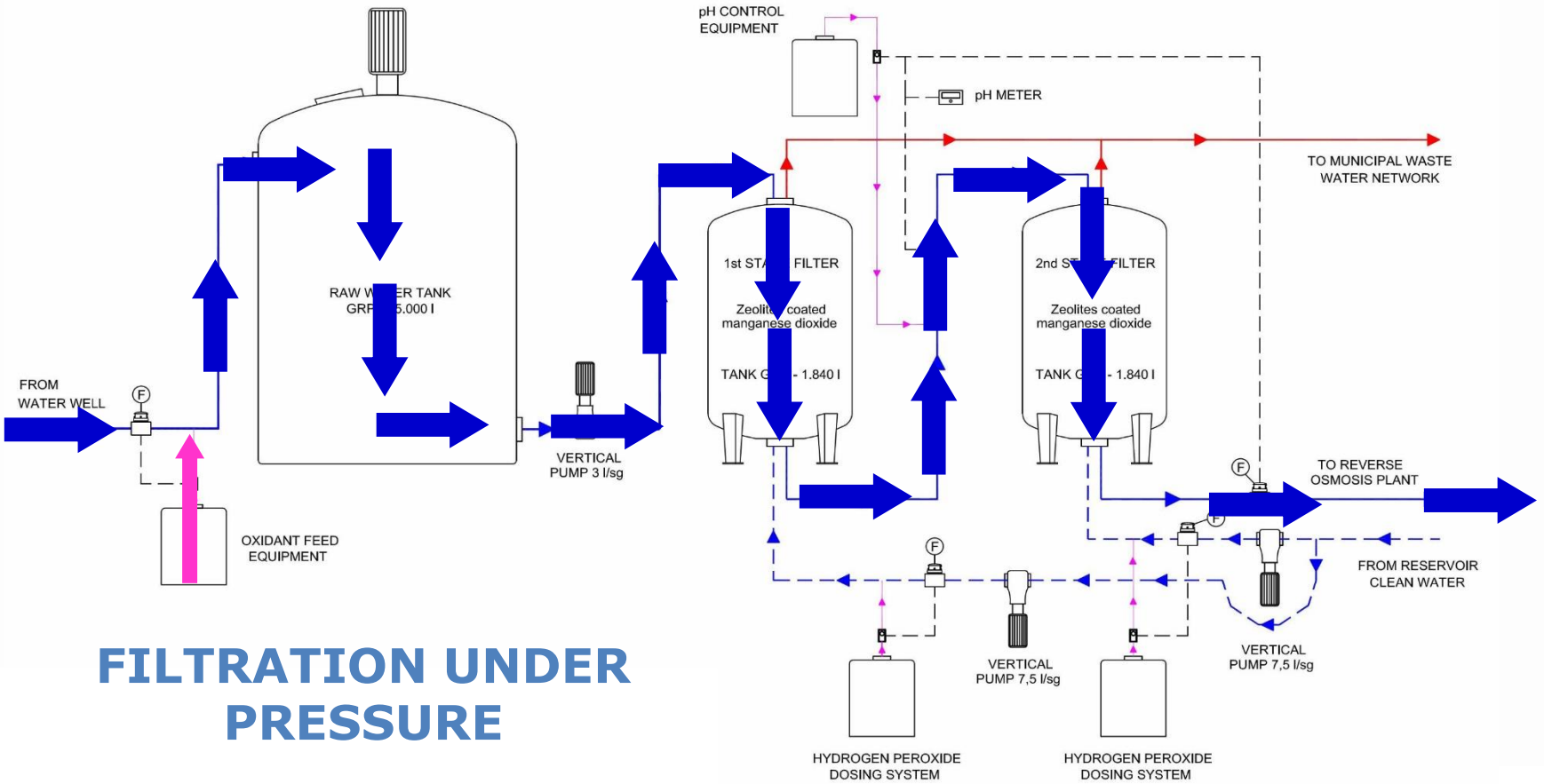
TAHAL

Radionuclide	Activity (Bq/L)	% TID
^{234}U	0.392±0.043	16,43%
^{235}U	0.010±0.002	
^{238}U	0.229±0.026	
^{226}Ra	0.061±0.004	
^{228}Ra	0.070±0.009	41,32%
^{210}Po	0.0030±0.0005	
^{210}Pb	0.026	15,35%
ID	0.0853 mSv/y	

Several wells in each location makes

Spanish plants description

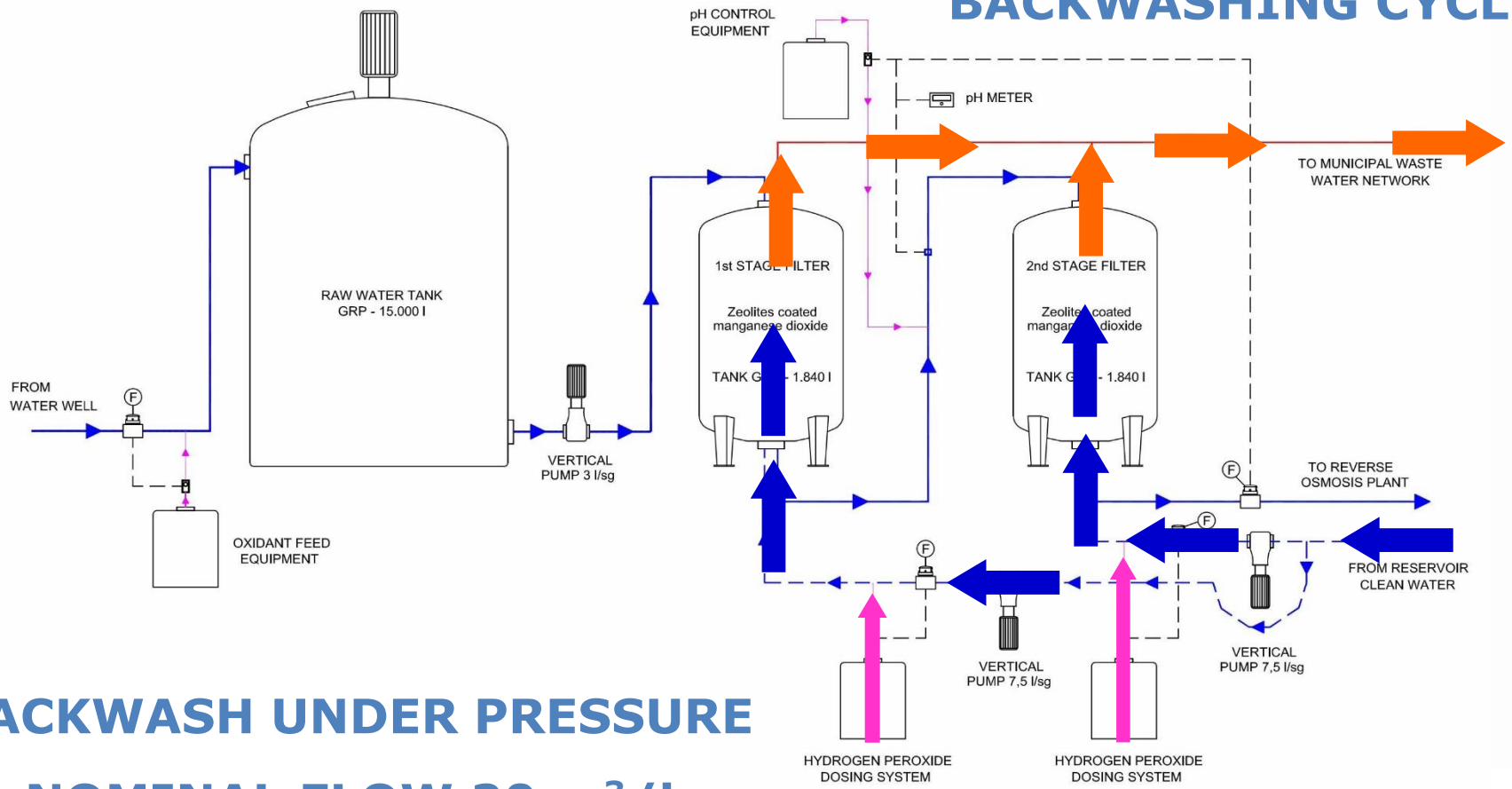
FILTRATION CYCLE



FILTRATION UNDER PRESSURE

NOMINAL FLOW 10 m³/h

BACKWASHING CYCLE



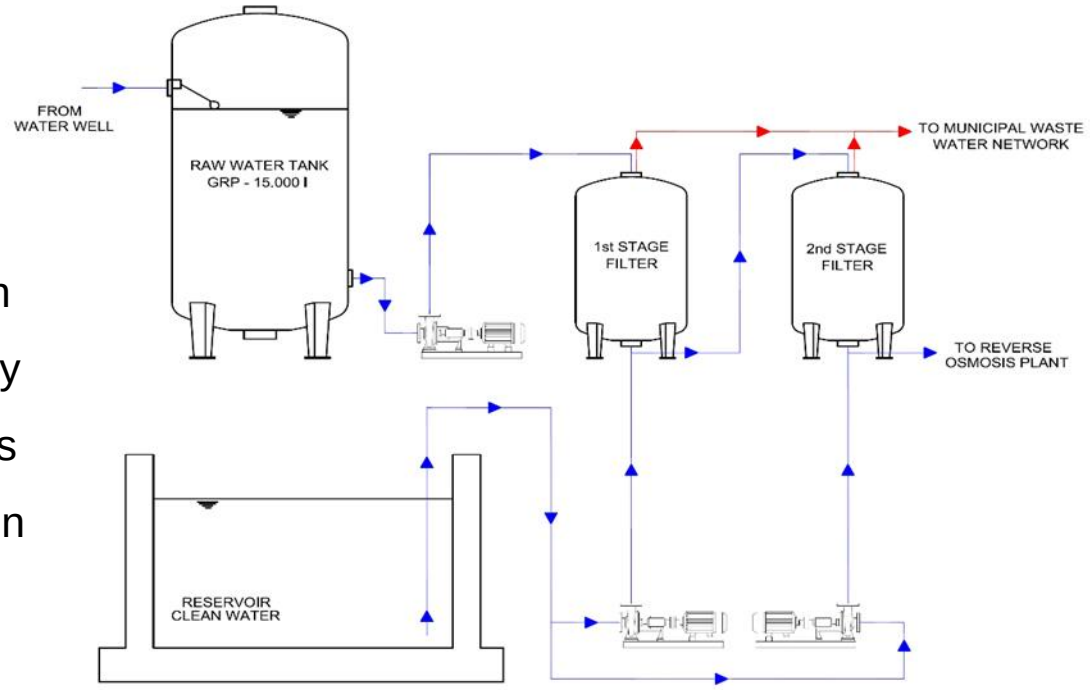
BACKWASH UNDER PRESSURE

NOMINAL FLOW 20 m³/h

Alchemia plants description

ALBOLODUY

- Small town with 621 registered inhabitants in 2018
- Clean water reservoir for backwash
- Raw water tank ensure flow stability
- Filtration and backwash with pumps
- Raw water tank provided of aeration
- Plant provided of reagents dosing pumps to control pH and ORP

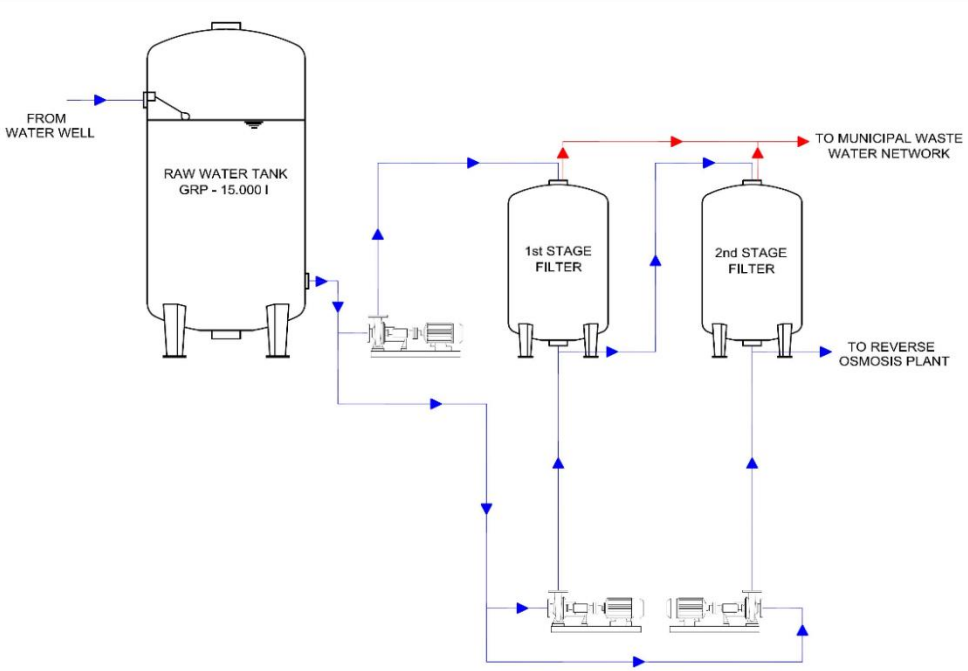


Alchemia plants description

BENIZALÓN

- Small town with 263 registered inhabitants in 2017

- No clean water reservoir for backwash due to several logistic reasons
- Raw water tank to ensure flow stability
- Filtration and backwash with pumps
- Backwash with raw water
- Important water restrictions during summer
- Raw water tank provided of aeration
- Plant provided of reagents dosing pumps to control pH and ORP

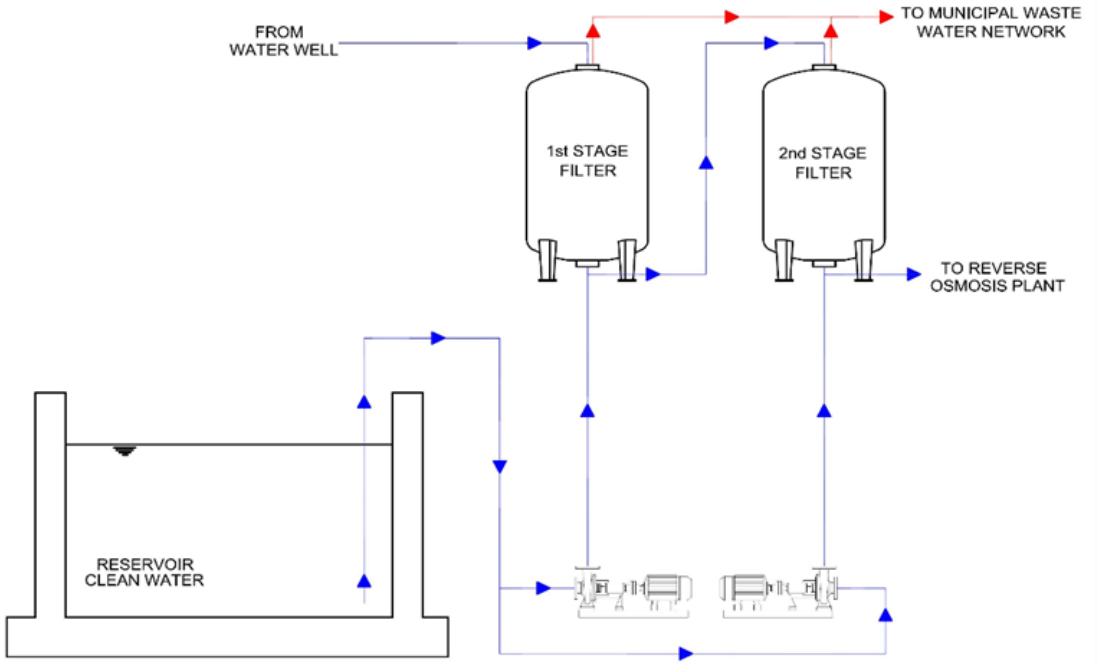


Alchemia plants description

TAHAL

- Small town of 346 registered inhabitants in 2017

- Wells 100 m higher than the plant location.
- Filtration operation can be carried out without pump.
- Reservoir clean water for backwashing
- Backwash with clean water
- Plant provided of reagents dosing pumps to control pH and ORP



Selecting the catalyst filter media

- **Alboloduy:** the main isotopes behind the ID is U234 and U238 (74,4%)

First filter: **Katalox light**, good efficience to eliminate Ra and U

Second filter: **Zeosorb** has been proved to efficiently remove Ra from water and be a good ion exchanger.

- ***Benizalon:*** the physico-chemical parameters comply with Spanish Law and the radiological characteristics of this water are the most complex, since the ID (0.34 ± 0.005 mSv/year) ***exceeds the value set by regulation by 3 times.*** **More contribution U (57,9) following Ra (30.9%)¡¡**

First filter: **Katalox light plus**, good efficience to eliminate Ra.

Second filter: **Hidrofer** has been proved to efficiently remove Ra and U by adsortion.

Selecting the catalyst filter media

- ***Tahal***: the feedwater of the Tahal DWTP exceeds the threshold limits for **Fe** concentration established by RD 314/2016, **Mn** is close to the limit and **Ra** isotopes (Ra-228 41.%) are the **main radionuclides** responsible for the ID **(59.7%)**

First and second filter:

Katalox Light (MnO_2 coated zeolite) because it is efficient in Mn and Ra removal.

Benizalon pilot plant

Tahal pilot plant

Selecting the catalyst filter media

DWTP	1 st filtration stage	2nd filtration stage
Alboloduy	KATALOX LIGHT WatchWater ® (Manganese dioxide coated zeolite)	ZEOSORB WatchWater ® (Zeolite)
Benizalón	KATALOX LIGHT PLUS Watch Water® (Manganese dioxide coated dolomite)	HIDROFERChiemiVall ® (Ferric Hydroxide)
Tahal	KATALOX LIGHT WatchWater ® (Manganese dioxide coated zeolite)	KATALOX LIGHT WatchWater ® (Manganese dioxide coated zeolite)

Filter-based pilot plants start-up, validation and operation

Compliance with drinking water quality standards, including radioactivity.

- To **check** the compliance with the drinking water **quality standards** of the treated water
- To **evaluate** the **NORM waste generation** during the operation of the three plants **and the efficiency** of the different strategies applied.

START-UP

- **Daily operation** mode will depend on the **water demand** and **availability by extractions of wells**.
- **Initial operational conditions** has been **established by** bed filtration material **suppliers** (10 m^3/h).
- **Choice and dosage of the reagents (oxidants for regeneration (H_2O_2), acids (HCl) and bases (NaOH/KCl). Start-up without reagents addition, no pH and ORP control.**
- Initial **regulation backwash operation** in line with rules of the bed-material **supplier**:

  - Benizalón: Daily backwash of 8 min (20 m^3/h) followed by settling time 2 min

  - **Alboloduy and Tahal:** Daily backwash of 10 min (20 m^3/h) followed by settling time 5 min

Results
Water analysis

ALBOLODUY

Filter-based pilot plants start-up, validation and operation

Compliance with drinking water quality standards, including radioactivity.

ALBOLODUY	Radionuclides	Inlet (B)	Outlet (T2)	Removal %	ID INLET mSv/y	ID OUTLET mSv/y	ID REDUCTION %
17/05/2019	U-238 (Bq/l)	0,2160	0,2360	-9,26	**0,0158**	**0,0161**	**-2,32**
	U-234 (Bq/l)	0,2160	0,2290	-6,02			
	Ra-226 (Bq/l)	0,0046	0,0009	**80,43**			
	Ra-228 (Bq/l)	nd	nd	nd			
11/11/2019	U-238 (Bq/l)	0,204	0,190	6,86	**0,0147**	**0,0138**	**5,89**
	U-234 (Bq/l)	0,204	0,199	2,45			
	Ra-226 (Bq/l)	0,003	0,002	**33,33**			
	Ra-228 (Bq/l)	nd	nd	nd			

As can be observed, the reduction of U234 and U238 is negligible. Nevertheless, Ra226 shows better behaviour because of the adsorption on the filter material. ORP and pH control turn into critical keys to ensure the coprecipitation of U with Fe and Mn.

TAHAL

Filter-based pilot plants start-up, validation and operation

Compliance with drinking water quality standards, including radioactivity

TAHAL	Radionuclides	Inlet (B)	Outlet (T2)	Removal %	ID INLET mSv/y	ID OUTLET mSv/y	ID REDUCTION %
17/05/2019	U-238 (Bq/l)	0,37	0,24	35,14	**0,0916**	**0,0316**	**65,47**
	U-234 (Bq/l)	0,56	0,36	35,71			
	Ra-226 (Bq/l)	0,091	0,0014	**98,46**			
	Ra-228 (Bq/l)	0,081	0,021	**74,07**			
11/11/2019	U-238 (Bq/l)	0,910	0,570	37,36	**0,1171**	**0,0651**	**44,38**
	U-234 (Bq/l)	1,160	0,710	38,79			
	Ra-226 (Bq/l)	0,061	0,019	**68,85**			
	Ra-228 (Bq/l)	0,066	0,034	**48,48**			

In this case, good reduction are obtained for both, uranium and radium isotopes. The indicative doses of this water influent is close to the limit. With the treatment safe water is achieved. ORP and pH control turn into critical keys to ensure the coprecipitation of U with Fe and Mn.

BENIZALON

Filter-based pilot plants start-up, validation and operation

Compliance with drinking water quality standards, including radioactivity.

BENIZALON	Radionuclide	Inlet (B)	Outlet (T2)	Removal %	ID INLET mSv/y	ID OUTLET mSv/y	ID REDUCTION %
17/05/2019	U-238 (Bq/l)	2,500	1,500	40,00	**0,2923**	**0,1358**	**53,54**
	U-234 (Bq/l)	3,600	2,100	41,67			
	Ra-226 (Bq/l)	0,090	0,007	**92,78**			
	Ra-228 (Bq/l)	0,125	0,020	**84,00**			
			Outlet (T1)				
11/11/2019	U-238 (Bq/l)	0,930	0,600	35,48	**0,2053**	**0,0694**	**66,18**
	U-234 (Bq/l)	1,620	0,940	41,98			
	Ra-226 (Bq/l)	0,177	0,022	**87,57**			
	Ra-228 (Bq/l)	0,160	0,023	**85,63**			

In this case, good reduction are obtained for both, uranium and radium isotopes. The indicative doses of this water influent exceed the limit. With the treatment safe water is achieved. ORP and pH control turn into critical keys to ensure the coprecipitation of U with Fe and Mn.

Results
Bed filter materials

Council Directive 2013/59/Euratom

Naturally occurring radionuclides materials

Values for exemption or clearance for naturally occurring radionuclides in solid materials in secular equilibrium with their progeny.

Natural radionuclides from the U-238 series (U234, Ra226 and others)	1 kBq / kg
Natural radionuclides from the Th-232 series (Ra228 and others)	1 kBq / kg

This directive has not yet been transposed to the Spanish legislation

NORM MANAGEMENT

In Spain, the **Order IET/1946/2013 of 17 October**, regulate the management of NORM

Characterization of the NORM wastes:

Radionuclide contents **lower than or equal** to the levels established in table 1 = **managed along conventional routes.**

In the case of **mixture of radionuclides**, the rule of the sum of the quotients between the concentration of the radionuclide present (Ci) and the applicable level (Cli) should be applied so that the following expression is verified:

$$\Sigma_{i=1,n} C_i/C_{li} \leq 1$$

Table 1. Levels applied to NORM waste in Bq/g, (Annex to the Order IET/1946/2013 of 17 October).

Radionuclide	All materials (Cli)
U-238 (sec) incl. U-235 (sec)	0,5
U natural	5
Th-230	10
Ra-226+	0,5
Pb-210+	5
Po-210	5
U-235 (sec)	1
U-235+	5
Pa-231	5
Ac-227+	1
Th-232 (sec)	0,5
Th-232 (sec)	5
Ra-228+	1
Th-228+	0,5
K-40	5
(sec):radionuclide in secular balance with all its descendants. (+): radionuclide in secular balance with its short-lived descendants.	

Assessment of NORM generation and management opportunities, including filters regeneration.

- To ***evaluate*** *the* ***NORM waste generation*** during the operation of the three plants and the efficiency of the different strategies applied.
- To ***study and evaluate*** filter cleaning strategies and regeneration with new reagents.

NORM index based on Order IET/1946/2013 of 17 October. Limit value = 1.

	May 2019		November 2019 Before Backwash		November 2019 After Backwash	
	Filter 1	Filter 2	Filter 1	Filter 2	Filter 1	Filter 2
Alboloduy	0,204	0,16	0,298	0,1599	0,29	0,1527
Benizalón	0,99	1,033	0,189*		0,155*	
Tahal	1,388	0,354	8,822*	0,772*	7,996*	0,75*

* NORM index calculated only with Rd 226 and Rd 228 concentrations

Results
Water & Energy consumption

ALCHEMIA PLANTS vs RO PLANTS

ALCHEMIA PLANTS vs RO PLANTS

Data collected between 12/2019 and 01/2020

WATER CONSUMPTION	ALBOLODUY	BENIZALÓN	TAHAL
ALCHEMIA PLANT WATER CONSUMED (m3)	18412,70	553,60	17344,00
ALCHEMIA PLANT DRINKING WATER PROCUCED (m3)	16787,60	466,20	15291,80
REVERSE OSMOSIS PLANT WATER CONSUMED (m3)	60922,46	3812,50	15658,00
REVERSE OSMOSIS PLANT DRINKING WATER PROCUCED (m3)	35420,03	2329,90	10048,60
ALCHEMIA INDICATOR WATER CONSUMED (m3)/DRINKING WATER PROCUCED (m3)	**1,10**	**1,19**	**1,13**
REVERSE OSMOSIS INDICATOR WATER CONSUMED (m3)/DRINKING WATER PRODUCED (m3)	**1,72**	**1,64**	**1,56**
WATER REJECTION REDUCTION	**86,5%**	**70,5%**	**75,9%**

ALCHEMIA PLANTS vs RO PLANTS

Data collected between 12/2019 and 01/2020

ENERGY CONSUMPTION	ALBOLODUY	BENIZALÓN	TAHAL
KWH ALCHEMIA ENERGY CONSUMPTION	4.466,50	316,10	447,50
KWH REVERSE OSMOSIS ENERGY CONSUMPTION	39.702,20	2457,90	12277,60
ALCHEMIA PLANT DRINKING WATER PROCUCED (m3)	16.787,60	466,20	15291,80
REVERSE OSMOSIS PLANT DRINKING WATER PROCUCED (m3)	35.420,03	2329,90	10048,60
ALCHEMIA INDICATOR KWH ENERGY CONSUMPTION/DRINKING WATER PROCUCED (m3)	**0,27**	**0,68**	**0,03**
REVERSE OSMOSIS INDICATOR KWH ENERGY CONSUMPTION/DRINKING WATER PROCUCED (m3)	**1,12**	**1,05**	**1,22**
Energy consumption reduction	**76,2%**	**35,7%**	**97,6%**

Conclusions and incoming tasks

CONCLUSIONS & NEAR – FUTURE TASKS

The preliminary results regarding radionuclides removal shows that the **plant operation need to be improved by controlling pH and ORP** adding reagents in order **to promote the coprecipitation of uranium with iron and manganese**. However, good behaviour has been observed for radium removal.

Taking into account the **Spanish regulation**, in this moment, **three** of the six **filter** could be considered as **NORM waste**, nevertheless, different conclusion can be achieve when apply the European Directive, in this case only the filter 1 of Tahal plant will be considered as NORM waste with Ra226 and Ra228 concentrations of 2,67 and 2,66 KBq/Kg, respectibely.

The filtration and backwash operation need to be optimized **to promote coprecipitation rather than adsorption** of radionuclides in the filter material in order to **increase the filter's life avoiding turn into NORM waste.**

Regarding the hydraulic operation, a **stable operation** of the plants has been achieved due to the optimal design and construction. In this sense, **high water (≈80%) and energy (≈ 85%) savings** compare with RO **have been also demonstrated**.

TOWARDS A SMART & INTEGRAL TREATMENT OF NATURAL RADIOACTIVITY IN WATER PROVISION SERVICES

Thank you very much for your attention!!!

Tänan teid väga tähelepanu eest!!!

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F. Javier Martínez Rodríguez
José L Casas López