ZERO BRINE

D4.1 Characterization of wastewater produced in the production process of precipitated silica

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Deliverable D4.1	Characterization of wastewater produced in the production process
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[1] **R**=Document, report; **DEM**=Demonstrator, pilot prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other
[2] **PU**=Public; **CO**=Confidential, only for members of the consortium (including the Comission Services), **CI**=Classified

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1. Introduction

The ZERO BRINE project aims to facilitate the implementation of the Circular Economy package and the SPIRE roadmap in various process industries by developing necessary concepts, technological solutions and business models to redesign the value and supply chains of minerals and water while dealing with present organic compounds in a way that allows their subsequent recovery. This is achieved by demonstrating new configurations to recover these resources from saline impaired effluents generated by process industries, while eliminating wastewater discharge and minimising environmental impact of industrial operations thorough brines.

One of the four demonstration sites of the project will be located at Industrias Químicas del Ebro S.A. (IQE) in Spain. IQE Group is an industrial chemical group composed by three companies: DESILSA, SIMAL and Industrias Químicas del Ebro, S.A. IQE, which has its headquarters in Zaragoza, began its business activity in 1958. It is specialized in basic inorganic chemistry and manufactures sodium and potassium silicates, metasilicate, zeolites, sodium and potassium aluminates, aluminium sulphate, precipitated silica, aluminium silicate and amorphous aluminium hydroxide.

IQE has an important commitment to collaborate with its clients and to invest more and more in research, development and innovation. Its main asset is its young and dynamic team, which is the basis of its successes and it also ensures the permanence of IQE as a leader in its sector. IQE manufactures their products at different plants and it covers a wide range of physicochemical properties that make their products crucial ingredients in many applications and consequently in markets like detergents, tires, construction, human and animal food, paints, varnishes, agriculture, wastewater and industrial water treatment, the paper industry, rubber, pharmaceuticals, ceramics, etc. The markets of IQE are located primarily in the European Union and North Africa. Nowadays, Turkey and Middle East, Asia or South America are expansion areas. IQE commits to a continuous improvement of their activities and processes in order to satisfy the expectations of their customers in quality and services.

Due to IQE productive activity, high amounts of waste streams with high salinity are produced. The management of these streams has a high environmental impact and an elevated cost is associated to their management. This cost is related to the discharge of these streams to be treated in a wastewater treatment plant. ZERO BRINE aims to evaluate an innovative treatment process for filtration and washing wastewaters in order to recover reagents and water to further valorize them either in the production process at IQE or in other industries. The implementation of the new treatment process will allow a reduction of costs derived from water consumption and wastewater management.

2. Objective

A thorough characterization of effluents resulting from the production activity of IQE is crucial in order to valorize the aqueous waste streams and to implement innovative management strategies more sustainable from an environmental and economical point of view.

The main objective of the subtask 4.1.1 from WP4 is to characterize the wastewater generated at IQE. The characterization has been focused on determining the concentration of main components such sodium and sulphate as well as trace elements such as aluminum, iron and silica that can produce scaling problems during nanofiltration treatment.

3. Production processes

IQE has three main synthetic products in its production line: amorphous silica (REACH number: 01-2119379499-16-0058), amorphous aluminum silicate (REACH number: 01-2119429887-22-0009), and amorphous aluminum hydroxide (REACH number: 01-2119529246-39-0005).

Each of these three main products are produced through a very similar production process which is schemed in Figure 1.

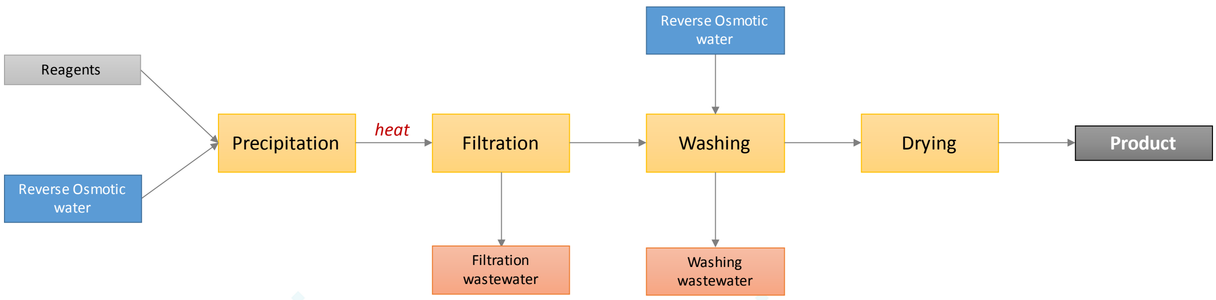

Figure 1. Production process of the three main products at IQE.

Firstly, the corresponding reagents and osmotic water are brought together to form a precipitate (raw product). The mixture is heated at a set temperature, which is different for each product and, later, filtered. Filtering generates filtration wastewater that has a high salinity. Afterwards, the precipitate is washed with reverse osmotic water and, thus, washing wastewater is generated. Both streams are mixed and treated in a wastewater treatment plant. Finally, the production process ends with the drying of the product. Quantities of water used and wastewater produced at the production process of each of the three main products are presented in Table 1.

Table 1. Process conditions for each of the main products in relation with Figure 1.

	Precipitated Silica	Aluminium sodium silicate	Aluminium hydroxide
Reverse Osmotic water for reaction (m^3/day)	919	112	116
Filtration wastewater (m^3/day)	840	121	186
Washing wastewater = Reverse Osmotic water (m^3/day)	1,506	934	3,158

Taking into account the chemical reagents used in the production processes, the high salinity of the effluents is expected to be due mainly to sodium and sulphate. Moreover, due to the composition of raw materials wastewater could contain Si, Al and Fe, which can cause scaling problems during the nanofiltration stage. Scaling can be related to the formation of precipitates (Al, Fe) or the formation of amorphous silica (Si) that can disturb the performance of the membranes.

It is as well noteworthy from Table 1 that reverse osmotic water consumption is high. Reverse Osmotic water is produced treating well water with a reverse osmosis system.

Table 2 presents the characterization of physicochemical parameters of the effluents at IQE in a previous project. It is seen that the high salinity of the wastewater effluents, as foreseen previously, is due to sodium, chloride and sulphate.

Table 2. Composition of the target effluents provided by IQE. (n.d. =not determined)

Parameter	Units	Well water	Reverse Osmotic water	Osmosis Concentrate	Silica Filtration wastewater	Silica Washing wastewater	Aluminium hydroxide Filtration wastewater	Aluminium hydroxide Washing wastewater
pH	-	7.4	7.1	7.0	5.4	6.5	8.2	7.7
Hardness	°F	n.d.	0.99	368	n.d.	n.d.	n.d.	n.d.
Conductivity	$mS\cdot cm^{-1}$	4.6	0.16	14	33	4.0	85	1.4
Total Suspended Solids (SST)	mg/L	n.d.	n.d.	n.d.	1,005	153	2,880	12
Total Inorganic Carbon (TIC)	mg/L	n.d.	n.d.	228	<10	n.d.	623	n.d.
Na	mg/L	891	18	2,873	11,409	1,186	34,219	530
K	mg/L	36	15	88	82	33	59	36
Mg	mg/L	70	<10	177	7.0	<10	6.0	<10
Ca	mg/L	195	<10	1,038	5.0	<10	8.0	<10
Cl	mg/L	1,103	48	4,346	1,473	195	128	63
NO_3	mg/L	39	11	157	22	14	12	11
SO_4	mg/L	582	40	2,192	21,552	2,013	70,187	196

a. Methodology

Samples from filtration wastewater of each of the three products under study were obtained. In addition, taking into account that Silica is the most produced product, it was interesting for ZERO BRINE to also characterize the washing wastewater from the Silica production process. It is worth to mention, that at the beginning of the project filtration wastewater and washing wastewater were collected separately. IQE performed some changes in the management of these wastewaters, and currently both wastewaters are mixed.

So, samples containing a mix of filtration wastewater and washing wastewaters were also acquired for characterization.

From September 2017, samples from filtration wastewater and washing wastewater from silica production where obtained once a month. From January 2018, the mix of filtration wastewater and washing wastewaters was implemented and samples were obtained weekly. The production of Aluminium sodium silicate and Aluminium hydroxide is not continuous. Therefore, samples of these products were obtained concurrently with the production process.

Critical parameters for the further treatment of these effluents were determined. For example, sulphates (SO_4) are of great interest as they are contained in one of the reagents used in the production process and they can form precipitates with several cations (Fe, Al, Ba) as well as. Therefore, determination of sulphates is relevant for the recovery of such resource and therefore their removal to achieve a fresh water stream. Another parameter of interest is silicon (Si) either total or reactive as it can form a sort of gel on top on the membrane surface and lead to a blockage of the system. It is important to characterize its presence to introduce proper pre-treatments to the membrane system. The relevant parameters and analytical methods used for their analysis are detailed in Table 3.

Table 3. Description of the used analytical methods.

Parameter	Equipment	Standard/Method
pH	pHmeter, Crison GLP 22	ISO10523:2008
Conductivity	Conductimeter, Crison MM41	UNE EN 27888:1994
Turbidity	2100Qis Turbidimeter , Hach Lange	Nephelometric
Total Inorganic Carbon	3100 N/C, AnalytikJena	C/N analyzer
Cations (K, Na, Ca, Mg)	Aquion, Dionex	Ionic Chromatography
Anions (Cl, NO_3, SO_4)	ICS 2100, Dionex	Ionic Chromatography
Metals (Al, Si, Mn, Fe, Sr, Ba)	7500 CX, Agilent Technologies	ICP-MS
Reactive Si	UV-Vis 3500, Schimadzu	Spectrophotometric

b. Results

The physicochemical characterization of the five effluents under study is shown in Table 4.

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Table 4. Characterization of the target aqueous waste streams. (n/a = not applicable; SD =standard deviation; n=number of samples)

Product		Precipitated Silica						Aluminium sodium silicate		Aluminium hydroxide	
Effluent		*Filtration wastewater (n=4)*		*Washing wastewater (n=4)*		*Filtration + Washing wastewater (n=6)*		*Filtration wastewater (n=3)*		*Filtration wastewater (n=3)*	
Parameter	Units	Value	SD	Value	SD	Value	SD	Value	SD	Value	SD
pH	upH	6.1	0.6	6.4	1.1	4.8	1.3	8.9	0.3	7.9	0.1
EC	mS/cm	38.3	10.4	15.5	10.7	27.3	5.9	44.9	0.7	87.4	0.8
Turbidity	NTU	313	347	207	337	67.4	133	>800	n/a	>800	n/a
Cl	mg/L	1,655	1,028	523	449	1,759	498	1,262	26.8	161	40.4
NO_3	mg/L	14.4	3.1	11.3	3.66	11.8	0.61	13.0	2.60	17.1	0.10
SO_4	mg/L	23,612	6,598	8,511	7,114	16,468	4,451	30,085	71.8	87,083	1,265
K	mg/L	52	5.5	14	11	434	11	11	1.7	25	4.0
Na	mg/L	12,340	4,199	4,603	3,924	7,325	2,061	14,954	1,189	43,078	2,486
Ca	mg/L	16.2	9.2	<5.0	n/a	38.5	35.3	6.8	8.5	<2.0	n/a
Mg	mg/L	<12.5	n/a	<5.0	n/a	213	235	<12.5	n/a	<5.0	n/a
TIC	mg/L	<10	n/a	49.9	92.1	<5	n/a	22.3	5.8	502	16.4
Al	µg/L	468	510	173	189	2,272	2,876	20.0	14.1	2,450	70.7
Si total	mg/L	74.2	57.8	26.4	26.0	80.5	22.8	72.5	6.4	1.4	0.6
Si reactive	mg/L	64.3	50.2	24.1	24.0	77.1	23.0	65.5	2.1	<1.0	n/a
Mn	µg/L	112.5	18.9	34.75	37.11	278	182	<10	n/a	9.6	3.4
Fe	µg/L	215.0	343.8	215	390.26	855	712	11.5	2.1	<20	n/a
Sr	µg/L	532.5	213.3	195.5	208.61	495	431	430	368	31.5	3.5
Ba	µg/L	160.8	179.7	79.2	127.4	49.2	16.4	50.0	22.6	11.5	4.9

It can be observed that the main components are sodium and sulphate, with lower amounts of chloride. The variability observed in the concentration of these components is because their concentration varies during washing. First moments of washing produce an effluent with a higher content of ions than at the end of the process. In other words, variability is related with the timing the sample was taken.

The obtained results present concentrations of sulphate, sodium and chloride consistent with the data of a project conducted previously from IQE (Table 2). Sulphate and sodium are the most concentrated ions in all three products which makes them a suitable sub-product (Na_2SO_4) to be valorised.

Among the three products, it is clear, by the conductivity and the concentration of ions, that the production of aluminium hydroxide results in wastewater with the highest salinity. Therefore, it is considered that the effluents from this product are suitable to be directly treated by crystallization to separate water from sub-products instead of the membrane system. Nevertheless, the other two products need as well a reduction of turbidity before treated by nanofiltration system as the maximum turbidity allowed is 1 NTU. The relatively high concentration of Al, Fe and Si is of concern too, as they can cause scaling at the membrane system. They can form precipitates in form of oxides or gels that can block the surface of the membrane and therefore disrupt its performance. Therefore pre-treatment is required.

4. Conclusions

- Filtration wastewater of the three main products as well as washing wastewater and mixed filtration and washing wastewater from Silica production have been characterized to determine their physicochemical properties.

- Main ions in solution were sulphate and sodium, which come from the reagents used in the production process.

- Aluminium hydroxide wastewater is not considered for nanofiltration treatment and will be treated directly by crystallization to separate water and sodium sulphate.

- The presence of Al, Fe and Si as well as the high turbidity of the effluents are inconvenient for the treatment of the wastewater by nanofiltration. Therefore, a pre-treatment is required to make the effluents suitable for the membrane system.