



**Pilot technology for aerobic  
biodegradation of spent TMAH  
Photoresist solution in Semiconductor  
industries**

Prof. Eng.  
Francesco Vegliò



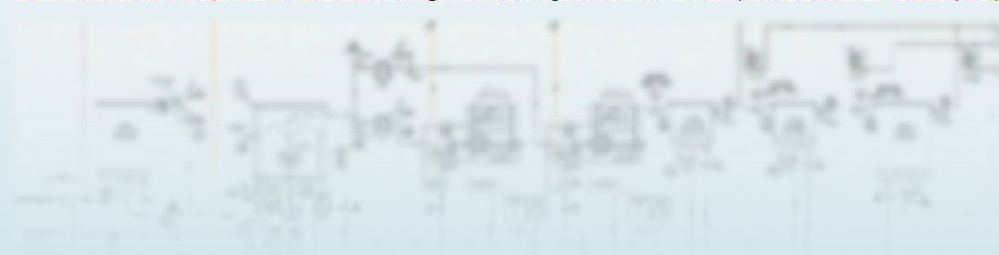
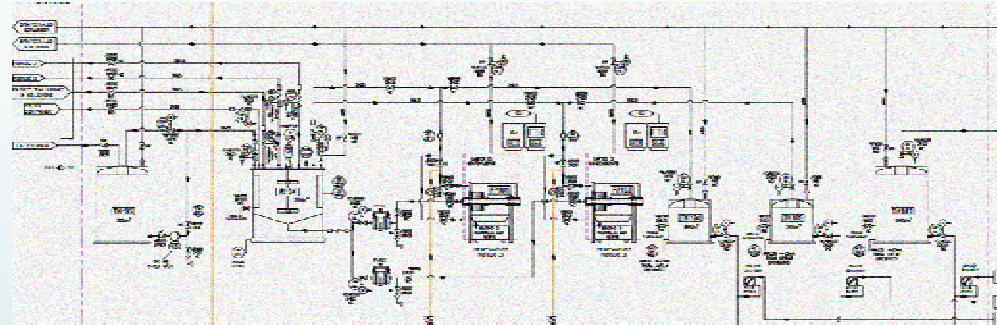
L'Aquila 31 Maggio 2017  
Aula Magna DSU  
Università degli Studi dell'Aquila

This research was financially supported by the European Union  
within the "LIFE BITMAPS" Project LIFE15 ENV/IT/000332.



# MAIN OBJECTIVES OF THE PROJECT

I. Design, construction and validation of a semi-industrial pilot plant enabling the treatment of spent photoresist/tetramethylammonium hydroxide (PR/TMAH), and other mixed solutions generated by the E&S (Electronic & Semiconductor) manufacturing processes.



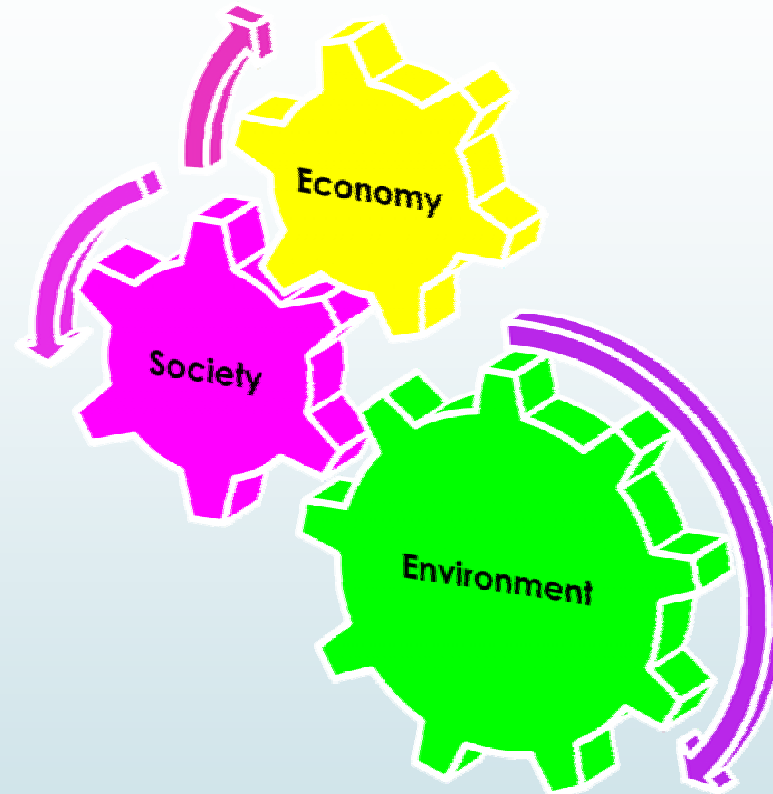
II. Demonstrate, at industrial scale, the biodegradation of TMAH to non-toxic biomass plus  $\text{NH}_3$  by using some specific savage microorganisms selected during the previous R&D phase.



# MAIN OBJECTIVES OF THE PROJECT



**III.** Prove the cost sustainability of the process



**IV.** Set up a more efficient water management approach proving that it is possible to reduce the net water consumption by saving water and evaluate the total reuse of treated wastewater in the company's industrial plant.



# PARTNERS OF THE PROJECT

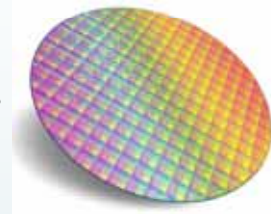
- ✓ **Lfoundry**  
**Industrial partner -Responsible**  
(Provided wastewater, support for all activities)
- ✓ **Univaq**  
**Scientific partner**  
(Laboratory tests of biodegradation,  
hydrocavitation and process analysis)
- ✓ **BME Biomaterials & Engineering S.R.L.**  
(Process analysis)
- ✓ **B.F.C. Sistemi Srl**  
(designs and constructs chemical plants and  
mechanical systems for industry)





# PROJECT DESCRIPTION

A large amount of wastewater containing tetramethylammonium hydroxide (TMAH) is generated each year in Europe by electronics' and semiconductor manufacturers



Because of the toxic properties of TMAH, for adequate protection of aquatic ecosystems, industrial streams containing TMAH require further treatment before they can be discharged into drainage systems

Current approaches to treatment of wastewater containing TMAH entail high costs for companies and negative environmental impacts.

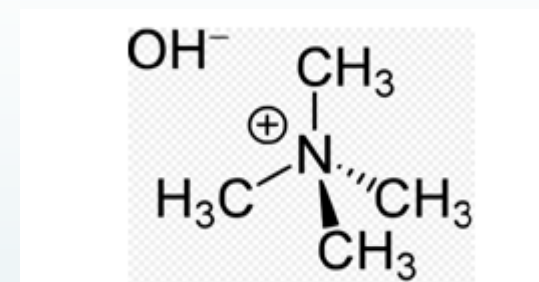


Development of an innovative process for the degradation of TMAH by biological treatment and hydrocavitation



# DANGEROUSNESS OF TMAH

During the process of realization of integrated circuits, tetramethylammonium hydroxide, also known as TMAH it is used.



This substance is a quaternary ammonium salt and it is a:

- compound odorless when pure
- corrosive and attack various plastics and rubbers
- turns out to be harmful to humans if ingested, inhaled or brought into contact with eyes or skin.

Environmental effects have not been studied at all: today is know that the TMAH is lethal to aquatic species (small fish, seaweed, shellfish)





## Laboratory activities

The banner features a light green header with the LIFE logo on the left. Below the header, on the left, is a map of Italy with a small LIFE logo icon. In the center, the text reads: "LIFE BITMAPS - Pilot technology for aerobic Biodegradation of spent TMAH Photoresist solution in Semiconductor industries" followed by the project number "LIFE15 ENV/IT/000332". On the right side of the banner is a photograph of a person wearing a white full-body protective suit and a mask, working with a large, dark, circular object, likely a semiconductor wafer.



## DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

### Materials and methods:

Biological tests are carried out in a cylindrical bioreactor BIOSTAT® B with a double glass and a capacity of 6 L, under batch condition with a control unit for setting parameters : temperature, velocity and Oxygen



Table 1: Operation parameters for the fermentator tests

Parameters	Value
Velocity	70 rpm
Temperature	25 °C
Oxygen	2- 5/L/min





# DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

## Materials and methods:

### Analysis

- COD (HACH-Lange kit: LCK 514)
- pH (HI254 pH-meter)
- TMAH (Ion Chromatograph Donex DX5000)
- ammonium ions (HACH-Lange kit: LCK 302) concentrations

### FEED OF THE BIOLOGICAL REACTOR

#### Wastewater

- TMAH
- PR (Photoresist) wich contains mainly 1-Methoxy-2-Propanol

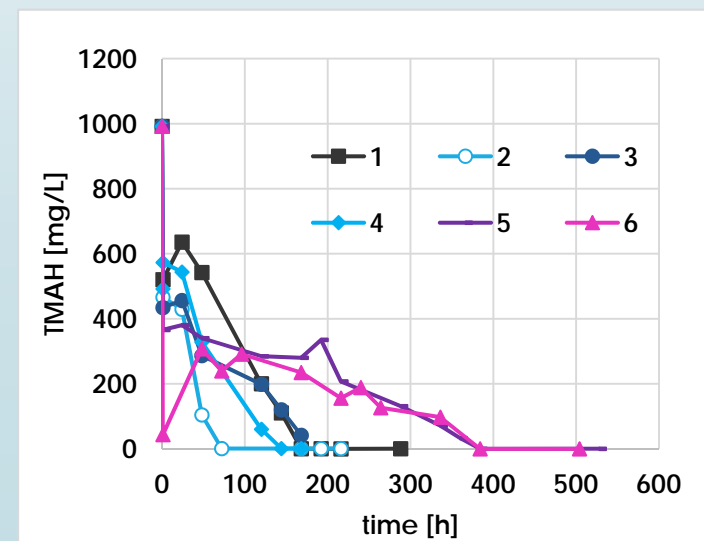
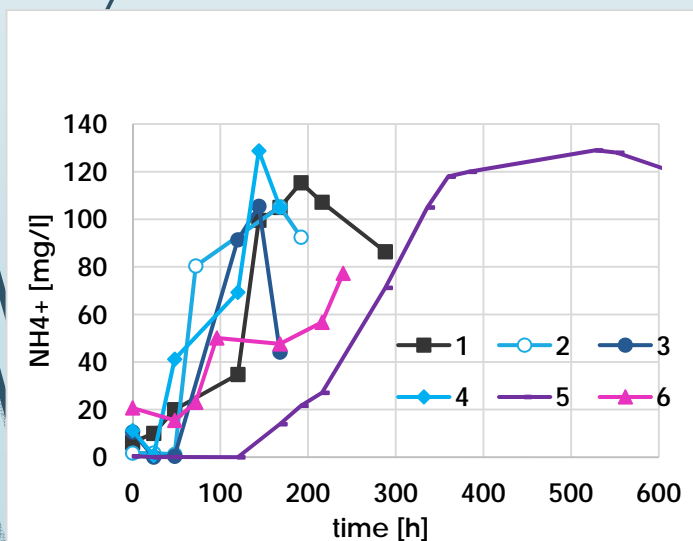
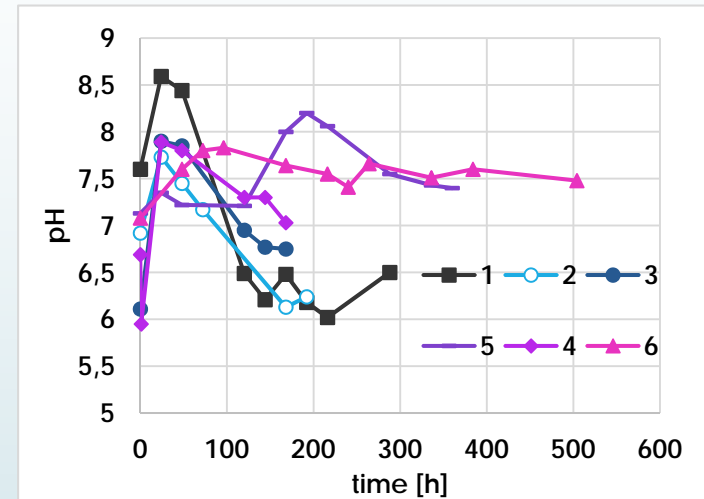
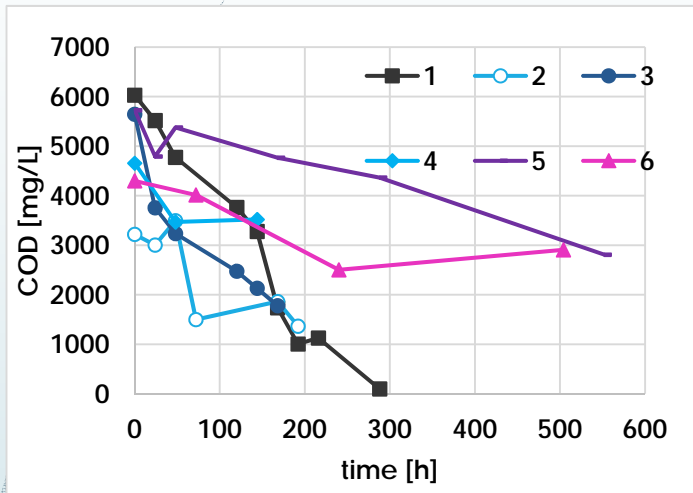
#### COMPOSITION OF THE CULTURE MEDIA

Substance	Concentration [g/L]
CuCl <sub>2</sub>	0.13
Na <sub>2</sub> MoO <sub>4</sub>	0.23
NaHCO <sub>3</sub>	0.82
K <sub>2</sub> HPO <sub>4</sub>	0.21
MgSO <sub>4</sub>	0.51
FeCl <sub>3</sub>	0.1
Yeast extract	0.01



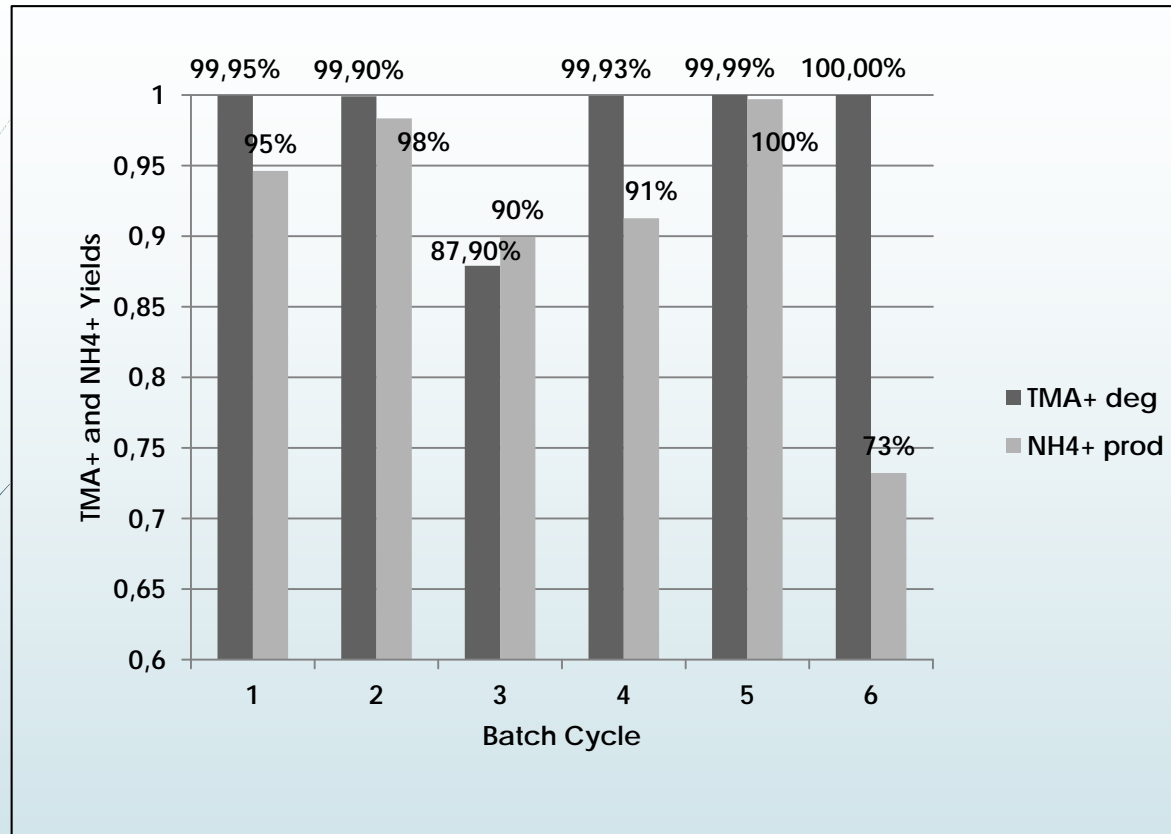
# DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

## Results:





## TMA+ degradation yield and NH<sub>4</sub><sup>+</sup> production yield

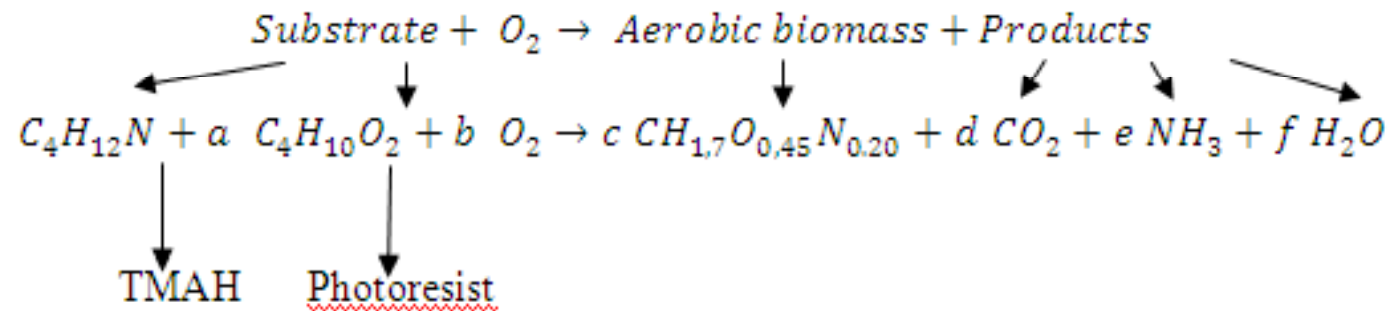


The experiments on wastewater have showed that biological treatment is able to remove TMAH with an efficiency greater than 99%, as TMAH removal yield, after about 6 days of process.



## DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

### Stoichiometry biomass growth:





## DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

$$\frac{dX}{dt} = \mu \cdot X \quad t = 0, \quad X = X_0$$

$$\frac{dS}{dt} = -\sigma \cdot X \quad t = 0, \quad S = S_0$$

$$\frac{dP}{dt} = \pi \cdot X \quad t = 0, \quad P = P_0$$

$$\mu = \mu_{MAX} \cdot \frac{S}{K_S + S}$$

$$\sigma = \frac{1}{Y_{X/S}^G} \cdot \mu + m$$

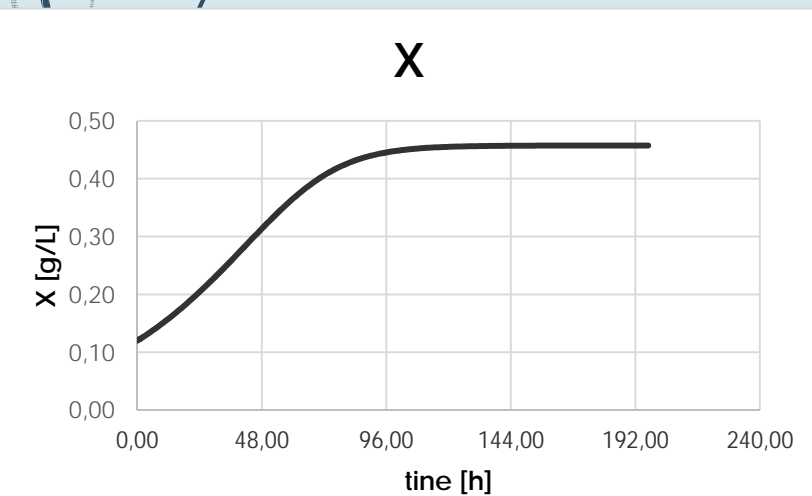
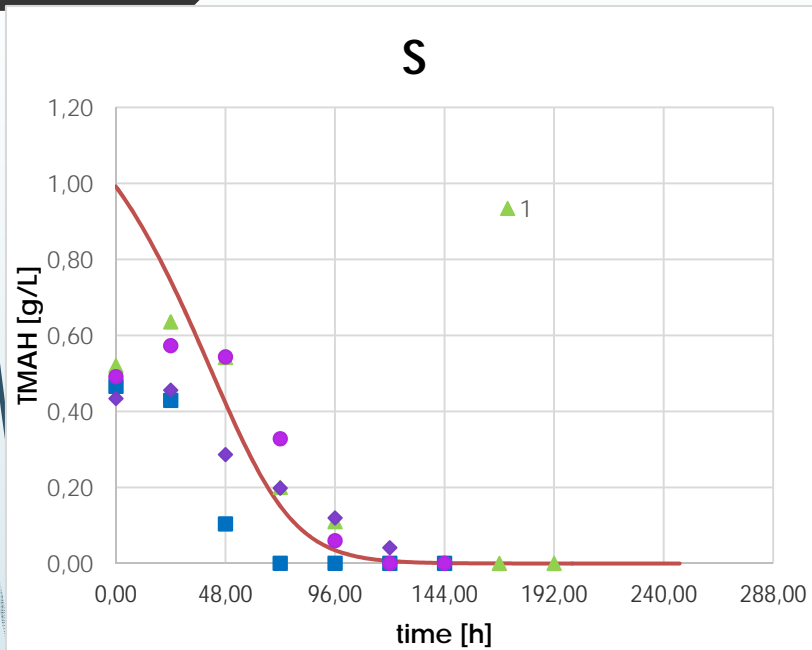
$$\pi = \alpha \cdot \mu + \beta$$

System resolution provides the following kinetic parameters:

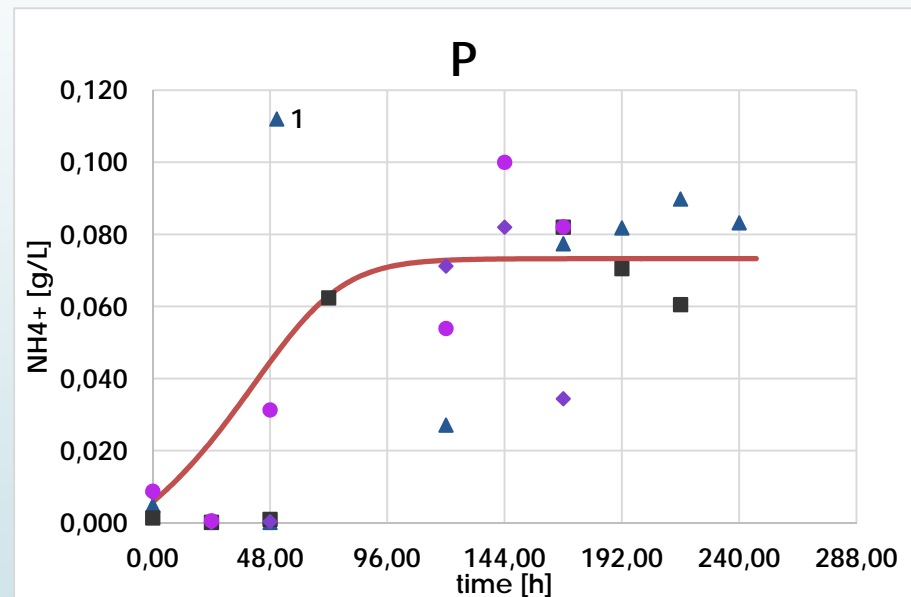
$$\mu_{MAX} \quad K_S \quad Y_{X/S}$$



# DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE



Solution of the system of equations for batch reactor



- $S_0 = 0,992$  g/L;
- $X_0 = 0,12$  g/L;
- $P_0 = 0,006$  g/L
- $\mu_{MAX} = 0,42$  h<sup>-1</sup>;
- $K_S = 0,8$  g/L;
- $Y_{X/S} = 0,34$





## Process Analysis

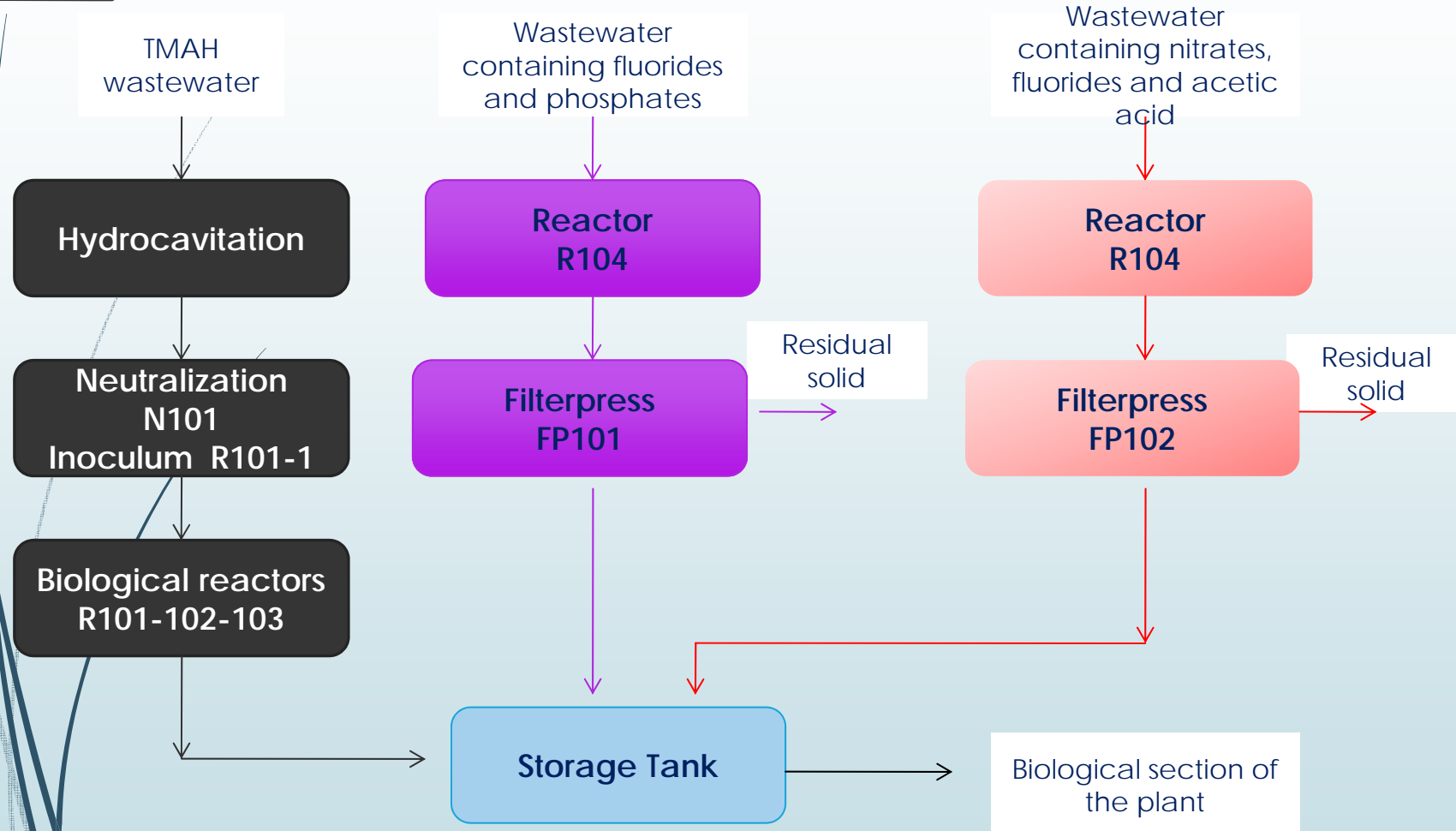


The same pilot plant treats other two types of wastewater that contain mainly fluorides, nitrates, acetic acid, .....

These wastewaters are treated using chemical-physical operations already validated in laboratory scale

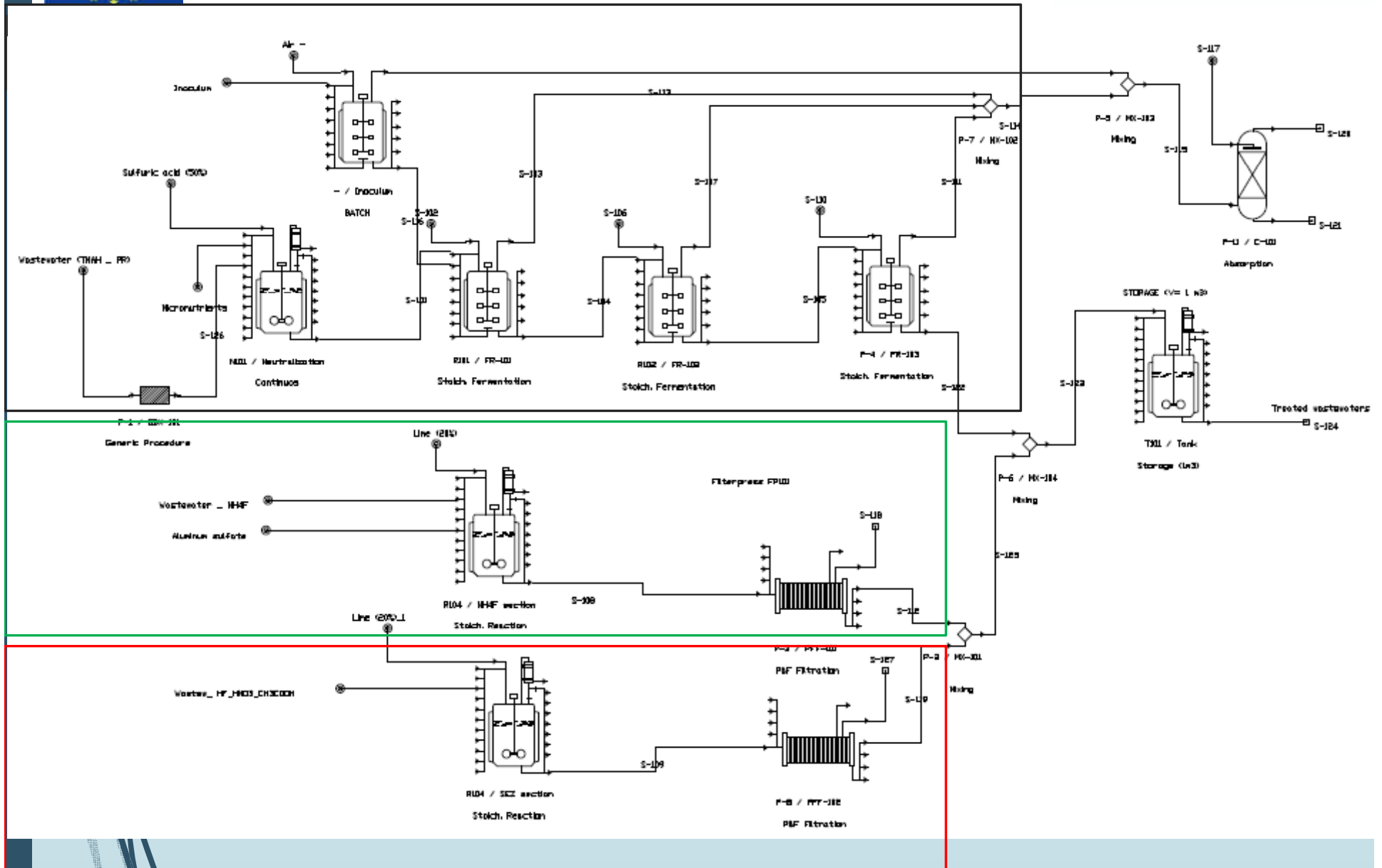


# Block scheme of the plant





# Simulation of the process





# Simulation of the process

Input - Wastewater	Unit
WastewaterTMAH Line 1	25 kg/h
Wastewater Line 2	60 kg/d
Wastewater Line 3	16 kg/d

Input – Reagents – Line 1	kg/h
Sulfuric acid for neutralization	0.1

Input – Reagents - Line 2	kg/d
Lime solution	21.84
Aluminum sulfate	2.4

Input – Reagents - Line 3	kg/d
Lime solution	9.29



# Simulation of the process



Output –Line 1		kg/h
Treated wastewater		27

Output– Line 2		kg/d
Treated wastewater		75
Residual solid		9

Output – Line 3		kg/d
Treated wastewater		24.6
Residual solid		1.28



## Simulation of the process

### Line 1

Removal yield of TMAH

1. 52% R101
2. 75% R02
3. 83% R103

Total yield: 98%

---

### Line 2

Reaction yields for the removal of the impurities ~100%

---

### Line 3

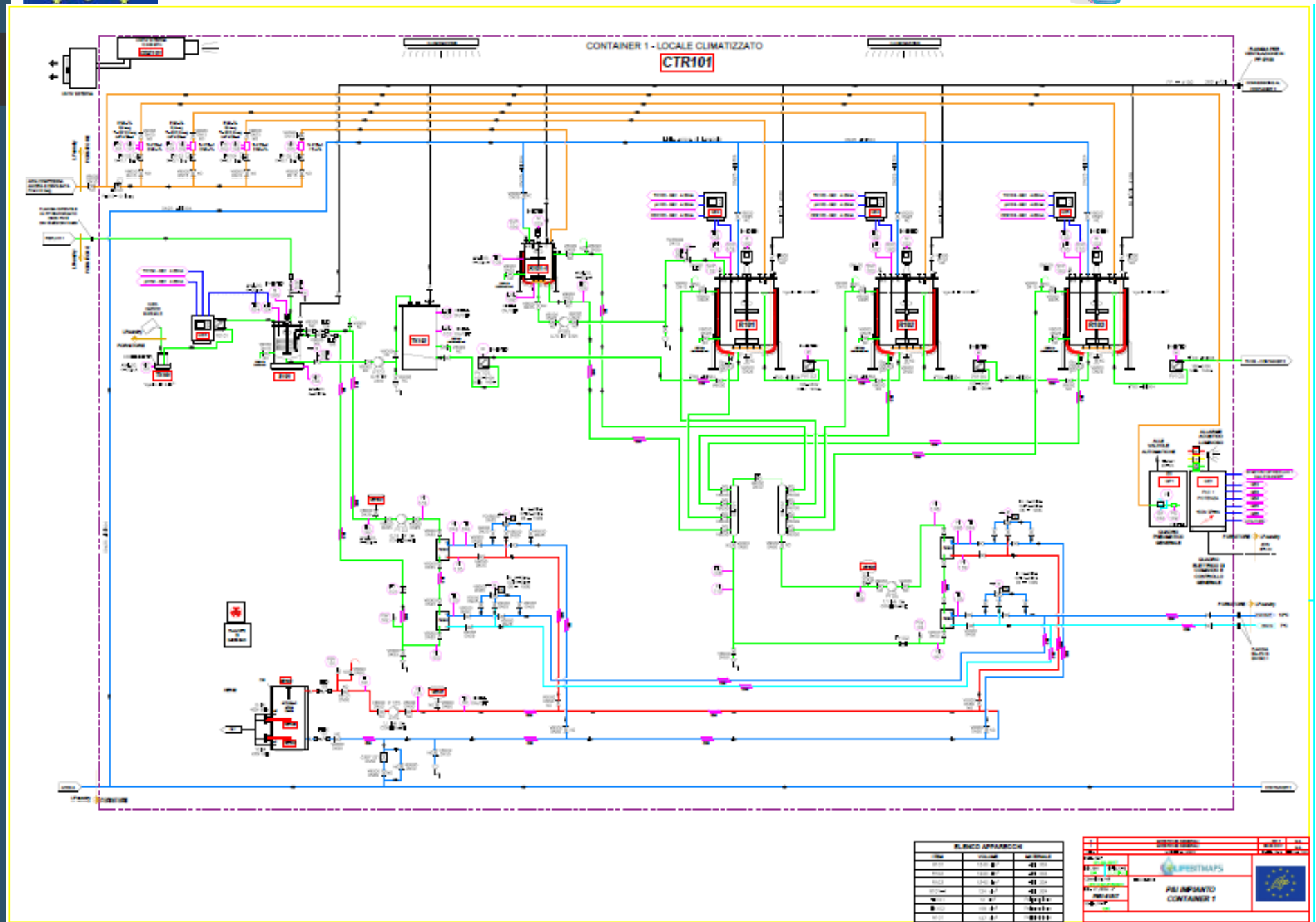
Reaction yields for the removal of the impurities ~100%





## EQUIPMENT SUMMARY (2017 prices)

Name	Type	Units	Standby/ Staggered	Size (Capacity)	Material of Construction	Purchase Cost (€Unit)
R101	Reactor	1	0/0	1,300.00 L	Plastic	5,000
R102	Reactor	1	0/0	1,300.00 L	Plastic	5,000
R103	Reactor	1	0/0	1,300.00 L	Plastic	5,000
N101	Reactor	1	0/0	33.80 L	Plastic	2,000
R101-1	Reactor	1	0/0	133.33 L	Plastic	2,000
R104	Reactor	1	0/0	130.00 L	Plastic	3,000
C-101	Absorber	1	0/0	1,178.10 L	Plastic	20,000
Tank	Reactor	1	0/0	1,000.00 L	Plastic	5,000
Cavitation	Generic Box	1	0/0	25.11 kg/h	CS	20,000
PFF-101-2	Plate & Frame Filter	1	0/0	0.51 m2	SS316	50,000



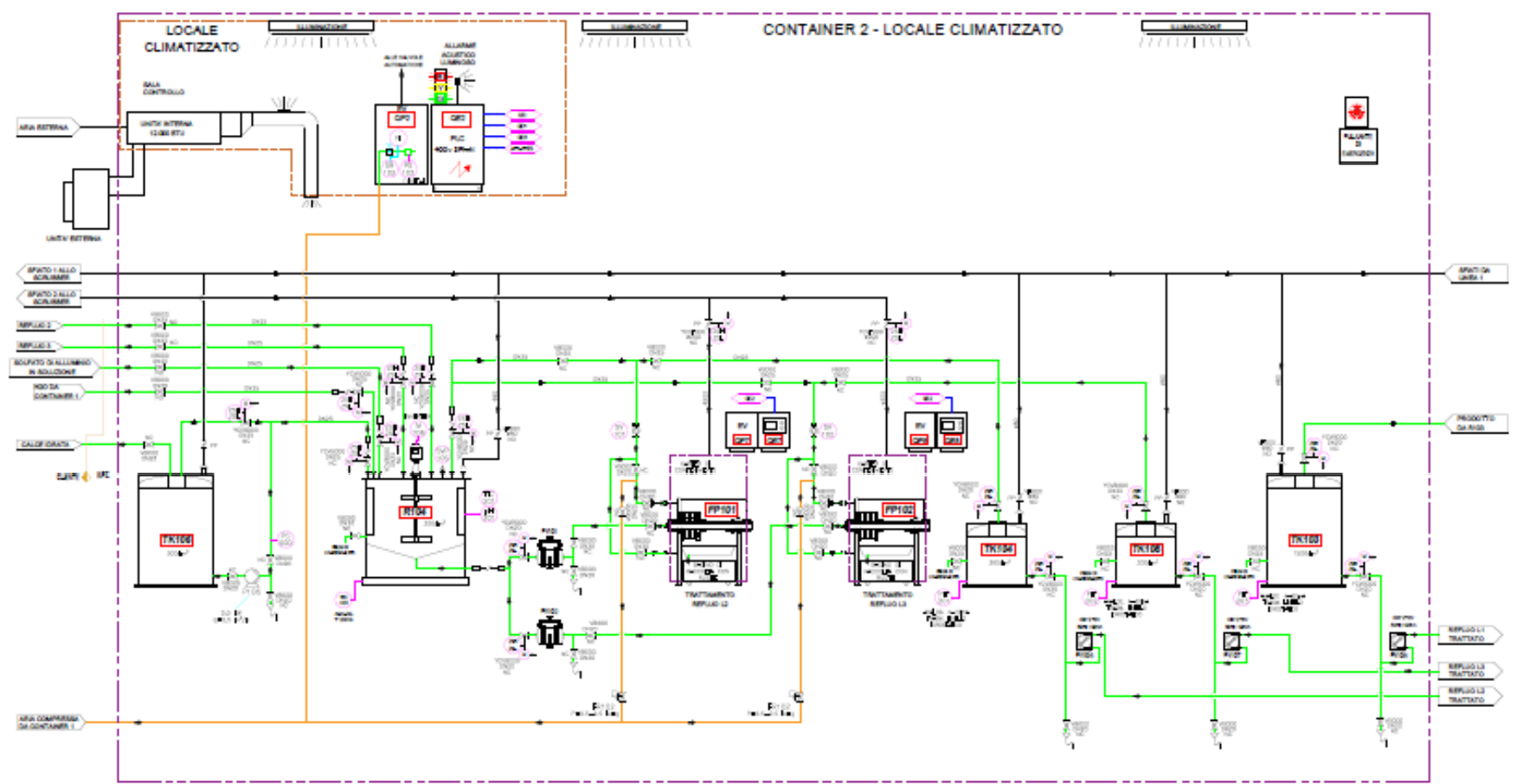
**LEGENDA APPROXIMATIVA**

LINEA	DESCRIZIONE	SEGNALAZIONE
RED	230V AC	~50 Hz
BLU	230V AC	~50 Hz
GRN	230V AC	~50 Hz
ORZ	230V AC	~50 Hz
...	...	...

**PROGETTO**

**BITMAPS**

**PIU' IMPIANTO CONTAINER 1**



**ELENCO APPARECCHIE**

ITEM	VOLUME	MATERIALE
TR104	200 m <sup>3</sup>	100 kg
TR105	200 m <sup>3</sup>	100 kg
TR106	200 m <sup>3</sup>	100 kg
TR107	200 m <sup>3</sup>	100 kg
TR108	200 m <sup>3</sup>	100 kg

I.C. 1 I.C. 2 I.C. 3 I.C. 4 I.C. 5 I.C. 6 I.C. 7 I.C. 8 I.C. 9 I.C. 10 I.C. 11 I.C. 12 I.C. 13 I.C. 14 I.C. 15 I.C. 16 I.C. 17 I.C. 18 I.C. 19 I.C. 20 I.C. 21 I.C. 22 I.C. 23 I.C. 24 I.C. 25 I.C. 26 I.C. 27 I.C. 28 I.C. 29 I.C. 30 I.C. 31 I.C. 32 I.C. 33 I.C. 34 I.C. 35 I.C. 36 I.C. 37 I.C. 38 I.C. 39 I.C. 40 I.C. 41 I.C. 42 I.C. 43 I.C. 44 I.C. 45 I.C. 46 I.C. 47 I.C. 48 I.C. 49 I.C. 50 I.C. 51 I.C. 52 I.C. 53 I.C. 54 I.C. 55 I.C. 56 I.C. 57 I.C. 58 I.C. 59 I.C. 60 I.C. 61 I.C. 62 I.C. 63 I.C. 64 I.C. 65 I.C. 66 I.C. 67 I.C. 68 I.C. 69 I.C. 70 I.C. 71 I.C. 72 I.C. 73 I.C. 74 I.C. 75 I.C. 76 I.C. 77 I.C. 78 I.C. 79 I.C. 80 I.C. 81 I.C. 82 I.C. 83 I.C. 84 I.C. 85 I.C. 86 I.C. 87 I.C. 88 I.C. 89 I.C. 90 I.C. 91 I.C. 92 I.C. 93 I.C. 94 I.C. 95 I.C. 96 I.C. 97 I.C. 98 I.C. 99 I.C. 100	DESCRIZIONE GENERALE CONTAINER 2   I.C. 101 I.C. 102 I.C. 103 I.C. 104 I.C. 105 I.C. 106 I.C. 107 I.C. 108 I.C. 109 I.C. 110 I.C. 111 I.C. 112 I.C. 113 I.C. 114 I.C. 115 I.C. 116 I.C. 117 I.C. 118 I.C. 119 I.C. 120 I.C. 121 I.C. 122 I.C. 123 I.C. 124 I.C. 125 I.C. 126 I.C. 127 I.C. 128 I.C. 129 I.C. 130 I.C. 131 I.C. 132 I.C. 133 I.C. 134 I.C. 135 I.C. 136 I.C. 137 I.C. 138 I.C. 139 I.C. 140 I.C. 141 I.C. 142 I.C. 143 I.C. 144 I.C. 145 I.C. 146 I.C. 147 I.C. 148 I.C. 149 I.C. 150 I.C. 151 I.C. 152 I.C. 153 I.C. 154 I.C. 155 I.C. 156 I.C. 157 I.C. 158 I.C. 159 I.C. 160 I.C. 161 I.C. 162 I.C. 163 I.C. 164 I.C. 165 I.C. 166 I.C. 167 I.C. 168 I.C. 169 I.C. 170 I.C. 171 I.C. 172 I.C. 173 I.C. 174 I.C. 175 I.C. 176 I.C. 177 I.C. 178 I.C. 179 I.C. 180 I.C. 181 I.C. 182 I.C. 183 I.C. 184 I.C. 185 I.C. 186 I.C. 187 I.C. 188 I.C. 189 I.C. 190 I.C. 191 I.C. 192 I.C. 193 I.C. 194 I.C. 195 I.C. 196 I.C. 197 I.C. 198 I.C. 199 I.C. 200	I.C. 201 I.C. 202 I.C. 203 I.C. 204 I.C. 205 I.C. 206 I.C. 207 I.C. 208 I.C. 209 I.C. 210 I.C. 211 I.C. 212 I.C. 213 I.C. 214 I.C. 215 I.C. 216 I.C. 217 I.C. 218 I.C. 219 I.C. 220 I.C. 221 I.C. 222 I.C. 223 I.C. 224 I.C. 225 I.C. 226 I.C. 227 I.C. 228 I.C. 229 I.C. 230 I.C. 231 I.C. 232 I.C. 233 I.C. 234 I.C. 235 I.C. 236 I.C. 237 I.C. 238 I.C. 239 I.C. 240 I.C. 241 I.C. 242 I.C. 243 I.C. 244 I.C. 245 I.C. 246 I.C. 247 I.C. 248 I.C. 249 I.C. 250 I.C. 251 I.C. 252 I.C. 253 I.C. 254 I.C. 255 I.C. 256 I.C. 257 I.C. 258 I.C. 259 I.C. 260 I.C. 261 I.C. 262 I.C. 263 I.C. 264 I.C. 265 I.C. 266 I.C. 267 I.C. 268 I.C. 269 I.C. 270 I.C. 271 I.C. 272 I.C. 273 I.C. 274 I.C. 275 I.C. 276 I.C. 277 I.C. 278 I.C. 279 I.C. 280 I.C. 281 I.C. 282 I.C. 283 I.C. 284 I.C. 285 I.C. 286 I.C. 287 I.C. 288 I.C. 289 I.C. 290 I.C. 291 I.C. 292 I.C. 293 I.C. 294 I.C. 295 I.C. 296 I.C. 297 I.C. 298 I.C. 299 I.C. 300	 I.C. 301 I.C. 302 I.C. 303 I.C. 304 I.C. 305 I.C. 306 I.C. 307 I.C. 308 I.C. 309 I.C. 310 I.C. 311 I.C. 312 I.C. 313 I.C. 314 I.C. 315 I.C. 316 I.C. 317 I.C. 318 I.C. 319 I.C. 320 I.C. 321 I.C. 322 I.C. 323 I.C. 324 I.C. 325 I.C. 326 I.C. 327 I.C. 328 I.C. 329 I.C. 330 I.C. 331 I.C. 332 I.C. 333 I.C. 334 I.C. 335 I.C. 336 I.C. 337 I.C. 338 I.C. 339 I.C. 340 I.C. 341 I.C. 342 I.C. 343 I.C. 344 I.C. 345 I.C. 346 I.C. 347 I.C. 348 I.C. 349 I.C. 350 I.C. 351 I.C. 352 I.C. 353 I.C. 354 I.C. 355 I.C. 356 I.C. 357 I.C. 358 I.C. 359 I.C. 360 I.C. 361 I.C. 362 I.C. 363 I.C. 364 I.C. 365 I.C. 366 I.C. 367 I.C. 368 I.C. 369 I.C. 370 I.C. 371 I.C. 372 I.C. 373 I.C. 374 I.C. 375 I.C. 376 I.C. 377 I.C. 378 I.C. 379 I.C. 380 I.C. 381 I.C. 382 I.C. 383 I.C. 384 I.C. 385 I.C. 386 I.C. 387 I.C. 388 I.C. 389 I.C. 390 I.C. 391 I.C. 392 I.C. 393 I.C. 394 I.C. 395 I.C. 396 I.C. 397 I.C. 398 I.C. 399 I.C. 400
--	---	--	--



# Thank You



Prof. Eng. Francesco Vegliò  
Department of Industrial  
Engineering, Information and  
Economy  
University of L'Aquila  
Montelucio di Roio

Contact:

[francesco.veglio@univaq.it](mailto:francesco.veglio@univaq.it)

Office tel: +39 0862 434223