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LIFE CYCLE INVENTORY (LCI)

The present report represents the fulfillment of points 1 and 2 of the sub-action C.1.2 of the European LIFE Project "Pilot technology for aerobic biodegradation of spent TMAH photoresist solution in semiconductor industries". More in detail, the action C.1 is dedicated to the "Environmental assessment of the project and of impact indicators in the specific phase", the sub-action C.1.2 is related to the Life Cycle Assessment, and the points 1 and 2 require the definition of goal and scope (point 1) and the life cycle inventory (LCI) of the process developed within the project (point 2). The whole report has the aim to respond to these requests, following the recommendation of ISO 14040:2006 norm; the Gabi 8.1 software was used for process databases.

1. Goal of the study

The general goal of the present study is the identification of the significant environmental loads connected with the pilot technology developed within the LIFE BITMAPS project. More specifically, the analysis will be carried out in order to achieve the following objectives:

- assessment of the pilot technology environmental load and identification of the critical points. This aspect is particularly important in order to address the ongoing activities towards the process sustainability.

- comparison of the innovative LIFE BITMAPS pilot technology with the current strategy of wastewater management, in order to highlight the most significant differences between the two choices.





The analysis is addressed both to the audience inside the project and to the external stakeholders. In the first case, the achieved results will be used to optimize the recycling process in terms of the environmental impact, and the LCA will be performed iteratively during the whole project. In the second case, the external stakeholders of the LIFE BITMAPS project are considered as a target audience (e.g. decision makers, public authorities).

2. Scope of the study 2.1 Functional unit

The pilot technology taken into account allows the treatment of three types of wastewater, characterized by a different composition, that need specific treatment, before the final disposal. The functional unit chosen for the analysis is the average wastewater annual production of the current process carried out by the project applicant. More in detail, the streams are the following:

- 1) Wastewater with TMAH and photoresist, with a flow rate of 5300 t/year (600 kg/h)
- 2) Wastewater with NH₄F, with a flow rate of 530 t/year (60 kg/h)
- Wastewater with nitrates, fluorides, phosphoric acid and acetic acid (SEZ) with a flow rate of 150 t/year (17 kg/h).

2.2 System boundaries

Figure 1 describes the system boundaries considered for the pilot technology operation, including the three lines of interest. The first flow is treated by a neutralization with sulfuric acid, followed by a biological treatment, that represents an innovation introduced by the project. Moreover, the innovative treatment of the second and the third lines consists of a precipitation using lime, with the addition of $Al_2(SO)_4$ *18H₂O, as coagulant, in the case of wastewater with NH₄F. Both operations include the final filtration for the separation of solid and liquid products. The water

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supply is included for the raw materials dilution and the liquid flows produced at the end of the three lines are treated in the biological reactor already available within the applicant facilities, before the final discharge. A separate operation is considered for the scrubber, necessary for the treatment of gaseous emissions, mainly containing ammonia. An average Italian power mix is chosen as energy source to feed all the main process blocks. As concerns the solid waste produced by the second and the third lines, the classification as either hazardous or not hazardous will be validated after the pilot plant tests; therefore, a sensitivity analysis will be carried out to assess the effect of waste characteristics on the whole environmental load of the process.



Figure 1 System boundaries for the processes carried out in the pilot plant for the wastewater treatment (Functional unit: annual flow rate, 5300 t/year TMAH, 530 t/year NH₄F, 150 t/year SEZ)





Figure 2 shows the system boundaries for the wastewater management strategy currently applied by the project applicant. The TMAH flow is treated by ion exchange and discharged; the resin is regenerated by a sulfuric acid solution, that is then neutralized with sodium hydroxide, and managed as not hazardous wastewater by external companies. The resin regeneration can be carried out for two year at most, thereafter the material is disposed as hazardous waste. On the other hand, NH₄F and SEZ flows are not processed inside the facilities of the applicant, and they are managed as hazardous wastewater, also in this case by external companies. In order to have an overview of current option environamental loads, the transport toward these companies is included within the system boundaries.



Figure 2 System boundaries for the current wastewater treatment

(Functional unit: annual flow rate, 5300 t/year TMAH, 530 t/year NH4F, 150 t/year SEZ)

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2.3 Assumptions and allocations

In order to solve the lack of details related to the production process of Al2(SO)4*18H2O within the reference database, we considered the reaction synthesis reported in Eq. 1, substituting the Al(OH)3 with the origin mineral bauxite. To overcome the problem of the impurities content, that makes it less concentrated than a pure raw material, we assumed double the stoichiometric amount of aluminum hydroxide.

 $2AI(OH)3 + 3H2SO4 + 12H2O \rightarrow AI2(SO4)3 *18H2O \quad (Eq.1)$

An additional assumption is that relative to the allocation of scrubber electric consumption. Indeed, starting from the daily data of energy consumption of the air treatment (22000 kWh per year), we decided to allocate this data, between the three lines, on the basis of the mass flow rates.

3. Life cycle inventory 3.1 Pilot innovative technology

Data reported in Table 1 summarize the input and output flows involved in the annual operation of the three lines of the LIFE BITMAPS innovative process.

With the aim to highlight the environmental load connected with the scrubber operation, its consumptions are firstly estimated separately. Thereafter, considering the real weight of each flow and the consequent air emissions to treat, the impacts connected with this operation are allocated between the three wastewater streams, according to the mass flowrate.

Table 1 Annual input and output flow rates involved within the LIFE BITMAPS innovative processes





Input	Output	
Line 1: Wastewater with TMAH and photoresist		
Wastewater, 5300 t/year	Treated wastewater, 5300 t/year	
Sulfuric acid (98%), 11 t/year		
Water, 10 t/year		
Electricity, 17,000 kWh		
Line 2: Wastewater with NH4F		
Wastewater, 530 t/year	Treated wastewater, 660 t/year	
Lime, 38 t/year	Solid waste, 80 t/year	
Water 150 t/year		
Al ₂ (SO) ₄ *18H ₂ O, 21 t/year		
Electricity, 1,400 kWh		
Line 3: Wastewater with nitrates	s, fluorides and acetic acid (SEZ)	
Wastewater, 150 t/year	Treated wastewater, 220 t/year	
Lime, 16 t/year	Solid waste, 11 t/year	
Water, 65 t/year		
Electricity, 400 kWh		
Scrubber		
Sulfuric acid (98%), 0.5 t/year	Wastewater, 1.5 t/year	
Water, 1 t/year	Ammonia, 78 kg/year	
Electricity, 22000 kWh		

These quantities are used to carry out the life cycle inventory, selecting as output information: the resources consumption, the deposited goods and the emissions in the two environmental compartments: water and air. Considering the criticality connected with the final solid waste





classification, which cannot be confirmed before the preliminary tests in the pilot plant, the first assessment considers a municipal solid waste with average characteristics referred to the European scenario (including the countries: AT, DE, IT, LU, NL, SE, CH).

As showed in Figure 3, the most critical aspect is the energy production mainly for the line 1 and the scrubber operation. The first line shows further effect on air emissions connected to the wastewater, which can be justified for both the energy demand and the produced gaseous emissions of biological treatment. On the other hand, the weight of the precipitation (in particular for the lime production) and the hazardous waste disposal of Line 2 is evident for the deposited goods compartment (Figure 3b).







Figure 3 Output of the inventory analysis relative to the innovative process, considering: a) the resources,b) the deposited goods, c) the emissions to water, d) emissions to air. The assessment compares the contribution of the three lines and the scrubber. (Functional unit: the annual flow rate).

With the aim to not consider the scrubber as a separate block but a step of each process line, its contribution was allocated on the basis of the input wastewater flow rate. As highlighted in Figure 4, the environmental load of air treatment is significant mainly for the Line 1 with a contribution variable between the 45 and the 30%, principally for the electricity supply.

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Figure 4 Output of the inventory analysis relative to the innovative process, after the scrubber contribution allocation, considering: a) the resources, b) the deposited goods, c) the emissions to water, d) emissions to air. The assessment compares the contribution of the three lines and the scrubber is allocated on the basis of each flow rate. (Functional unit: the annual flow rate).

3.2 The effect of solid waste classification

As explained before, a final classification of the produced waste is not possible, before the real tests on the pilot plant. For this reason, a sensitivity analysis was performed considering three different waste typologies.

Figure 5 shows the total impact, including the three lines of interest, evaluated by the different waste. The effect of the solid characteristics is evident in the comparison between the not hazardous HW1 and the two hazardous wastes (HW2 and HW3) with differences around 25%.





This difference increases up to 50% considering the deposited goods aspect. On the other hand, the gap between HW2 and HW3 is not significant for the resources and the emissions to water (Figures 5a, c), around 4%, but clearer for the deposited goods and the emissions to air, 55% and 25%, respectively (Figure 5b, d).



HW 1_EU-28: Municipal household waste (AT, DE, IT, LU, NL, SE, CH) on landfill

HW2_EU-28: Hazardous waste, C rich (Incineration, macroencapsulation, vitrification, transport and landfill)

HW3_DE: Hazardous waste, no C (Macroencapsulation and landfilling of inorganic hazardous waste)

Figure 5 Effect of three waste typology on the whole pilot plant impact (HW1: European municipal solid waste suitable, HW2: European hazardous waste, carbon rich, HW3: German hazardous waste, without carbon content. The evaluation was carried out considering: a) the resources, b) the deposited goods, c) the emissions to water, d) emissions to air. (Functional unit: the annual flow rate).





3.3 Pilot LIFE BITMAP technology vs. the current option

Considering the current process described in Figure 2, Table 2 summarizes the input and output flows, using the data supplied by the project applicant. In order to compare the innovative and the current option, the analysis was referred to the same quantities resulting from the functional unit chosen for the analysis (Paragraph 2.1).

Table 2 Annual input and output flow rates involved within the current processes

Input	Output	
Line 1: Wastewater with TMAH and photoresist		
Wastewater, 5300 t/year	Treated wastewater, 5300 t/year	
Sulfuric acid (98%), 32 t/year	Not haz. wastewater, 2100 t/year	
Sodium hydroxide, 31 t/year	Hazardous resin, 280 kg/year	
Deionized water, 2,000 t/year		
Electricity, 4000 kWh		
Resin, 280 kg/year		
Line 2: Wastewater with NH4	F (treated by external companies)	
	Hazardous wastewater, 530 t	
Line 3: Wastewater with nitrates	s, fluorides and acetic acid (SEZ),	
(treated by exte	ernal companies)	
	Hazardous wastewater, 150 t	

The current necessity of the treatment of wastewater (flow from neutralization of line 1

and streams from lines 2 and 3) by external companies, makes the transport a





significant contribution to consider in present LCI. In this regard, Table 3 summarizes the number and the distance of the annual trips for the streams transport.

Table 3 Number and distance of the trips towards the external companies for the current treatment of flowfrom neutralization of line 1 and streams from lines 2 and 3.

Line	Number of trips per year	Distances (km)
Line 1	50	366
Line 2	24	400
Line 3	7	230

Firstly, the evaluation focused on the current option (Figure 5), to assess the contribution of the three streams included in the system boundaries. The main criticality of sodium hydroxide production, within Line 1, is highlighted for all the considered environmental aspects. Moreover, in Figure 6 b (deposited goods) the weight of Line 2 and 3 is evident since the two streams are not treated at the plant, but they are sent to specific companies and treated as hazardous waste. In this regards, the whole contribution is due to the hazardous wastewater treatment, that covers, almost completely, the transport effect.







Figure 6 Output of the inventory analysis relative to the innovative process, considering: a) the resources, b) the deposited goods, c) the emissions to water, d) emissions to air. (Functional unit: the annual flow rate).

The results in Figure 7 compare the innovative and the current options. In this case, the whole environmental loads were assigned to each line for both the choices. The highest impact of the current process is evident for all the considered compartments. Indeed, the application of new technology allows the decrease of the effects, especially those connected with the Line 1, for the avoided use of sodium hydroxide.







■ TMAH and photoresist ■ NH4F ■ SEZ

Figure 7 Comparison between the current and the innovative options considering: a) the resources, b) the

deposited goods, c) the emissions to water, d) emissions to air. (Functional unit: the annual flow rate).

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