

Safety Analysis of Industrial Wastewater Pilot Plant for the Removal of Pollutants from Microelectronic Industry Effluents

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A technical safety analysis has been performed for the treatment of a real industrial wastewater plant. The process has been developed to remove organic and inorganic pollutants contained in the residual solutions from microelectronic industry, LFoundry srl (Avezzano, Italy). The treatment of three effluents (WW₁, WW₂ and WW₃) has been studied at the laboratory and pilot scale. WW₁ contained tetramethyl ammonium hydroxide (TMAH, on average 2 g/L), instead the WW₂ and the WW₃ contained nitrates, fluorides and acetic acid. TMAH effluent was aerobically treated by an activated sludge system, instead the second and the third wastewaters were chemically treated with lime in the presence of aluminum sulfates to precipitate the impurities. The experiments have been performed in batch and continuous mode and the results on lab scale have been used to design the equipment of the pilot plant. The plant has been realized in two 40 feet standard containers and can treat the three types of industrial effluents produced by LFoundry.

The safety analysis has been performed by using hazards and operability method (HAZOP) in order to identify the main hazards of the wastewater treatment and to assess an upgrading of the existing plant at the full scale. The pilot plant is almost completely automatic, this minimizes operator input and hence the probability of human errors during the operations performed directly in the plant, that could have more harmful consequences.

The analysis has been performed to point out the causes of failure, the consequences and the possible actions to identify and reduce the anomalies of the system. These activities have been performed within European Life Bitmaps Project (Grant Agreement N. LIFE 15 ENV/IT 000332).

1. Introduction

Tetramethyl ammonium hydroxide (TMAH, (CH₃)₄NOH) is an organic substance used for the production of semiconductors by microelectronics industry. This type of productive activity requires a large amount of ultra-pure water and use of important amount of chemical reagents, as TMAH, that at the end of the production cycle must be appropriately disposed of to avoid the dispersion of toxic substances in the environment and aquatic system. The microelectronics industry, as Lfoundry srl (Avezzano, Italy) produces a large amount of wastewater with relevant concentrations of inorganic compounds (as hydrofluoric, sulfuric, phosphoric, and nitric acid, ammonium hydroxide) and heavy metals such (as copper, iron, aluminum, etc.) and organic compounds. Traditional industrial processes are successful used for the removal of inorganic substances from wastewater (Jane Huang and Liu, 1999). On the contrary the removal of the organic compounds as TMAH is already an open issue. TMAH solutions (CAS NUMBER 75-59-2, where CAS Number is the registration number of the Chemical Abstracts Service) is a colourless to light yellow solutions and due to its highly alkalinity and toxic properties, there were several accidents of poisoning and deaths caused by TMAH, which is dangerous also in diluted formulations. TMAH is also toxic for water environment, the NOEC (No Observed Effect Concentration) to prevent chronic toxic effects on invertebrates (*Ceriodaphnia dubia*, *Daphnia magna*) is 0.025 mg/L (ECHA, 2020). As foreseen by the EU Water Framework Directive 2000/06/EC and taking into account other considerations, ISS (Italy National Health Institute) recommends keeping the discharge limits

below 0.4 mg/L in the drainage system and to ensure 0.2 mg/L thresholds in water bodies. Regional Agency for the Environment Protection of Abruzzo region has transposed the technical note of ISS and has recommended LFoundry to investigate viable solutions for reducing the TMAH concentration on its plant. TMAH effluent was aerobically treated by an activated sludge system, instead the second and the third wastewaters were chemically treated with lime in the presence of aluminum sulfates to precipitate the impurities.

The experiments have been performed in batch and continuous mode and the results on lab scale have been used to design the equipment of the pilot plant. The plant has been realized in two containers of 40 feet, ft (around 12 m). A technical safety analysis has been performed for the pilot plant to identify events that could cause a significant hazard for the workers and environment. The main intrinsically hazardous element of a biological system is the solution containing the bacteria (Pettauer et al. 1998) and in this specific case other sources of hazard are the dangerous substances (mainly TMAH effluent) for their toxicity.

Therefore, it is fundamental that the hazard potential of the industrial wastewater treatment is carefully identified. Usually, it is a failure of a component or a system that leads to a malfunction and consequently to conditions that may be hazardous. The safety analysis has been performed by using hazards and operability method (HAZOP) in order to identify the main hazards of the wastewater treatment and to assess an upgrading of the existing plant at the full scale. The safety study has been performed within European Life Bitmaps Project (Grant Agreement N. LIFE 15 ENV/IT 000332) (Life Bitmaps, 2020).

2. Methodology

2.1 Description of pilot plant

The pilot plant under investigation had been designed and built in Lfoundry site (Avezzano, Italy) for the treatment of TMAH effluent (WW_1) and other two industrial wastewaters contained acids and other substances (WW_2 and WW_3). After a laboratory scale optimization, it has been defined the technical solution including mass and energy consumptions to treat the three effluents. The solution adopted for TMAH wastewater has been a biological degradation carried out by adapted microorganism collected from activated sludge of the biological plant of the site. The bio-removal of TMAH had been studied on laboratory scale as demonstrated by scientific literature.

This research activity showed that TMAH is degraded by bacteria after an adaption time (Moretti et al., 2017; Innocenzi et al., 2019). For that, it has been decided to optimize the biological process for TMAH degradation and scale up on pilot scale in according to the goal of the Life Bitmaps project. For the other two effluents the solutions adopted have been chemical treatments by addition of precipitating agents. After treatment, the effluents can be safely sent to biological wastewater plant operating at the industrial scale. The Life Bitmaps pilot plant has been built in two containers installed at the Lfoundry site. After a design optimization for the processes, the first treatment section has been realized with three reactors in series having a capacity of 1.1 m³ aimed to achieve an aerobic biodegradation TMAH/PR (WW_1) within the Container1. Instead the section for the treatment of WW_2 and WW_3 is composed by a chemical reactor and a Filter-press. The first treatment line works in continuous mode with a maximum capacity of TMAH effluent of 25 L/h, while the other section works in batch mode treating WW_2 or WW_3 streams on alternate basis with a maximum capacity of 180 L/batch (Tortora et al., 2018; Innocenzi et al., 2018, 2019; Ferella et al., 2019).

The results of the pilot plant research showed that 99% of TMAH degradation has been obtained thorough the proposed treatment executed within the Container 1 with a process time of 192 hours. After that the treated effluent has been sent to the operating active sludge plant at the facility (featured by an additional process time of 36 hours) observing a further degradation for TMAH at its final discharge.

Figure 1 shows the block scheme of the wastewater treatment, instead some picture of the plant is reported in Figure 2.

Pilot plant has been analysed from a safety point of view. The results presented here derive from a preliminary study, that will be the groundwork for a further implementation of the project that should be realized at the full scale. A hazard and operability (HAZOP) investigation may identify a number of deviations from the intention, some of which may be judged as remarkable and having potentially hazardous consequences. Any absent safety measures should be subsequently implemented both by proposal for the industrial plant design, and by organisational measures to be included into the standard operating procedures (SOP).

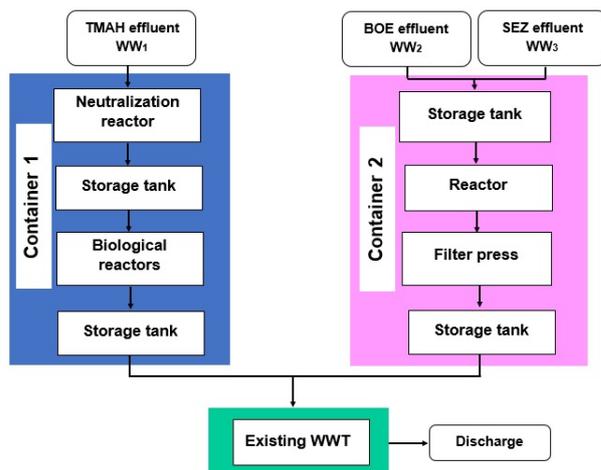


Figure 1: Block scheme of the pilot plant



Figure 2: Some pictures of the pilot plant

The pilot plant considered in this study can be viewed as a standard installation of low complexity. HAZOP method has been chosen to carry out this preliminary technical safety analysis. It provides a structured and detailed examination of all parts of the plant. The analysis requires the in-depth knowledge of the process, the study of the Piping and instrumentation diagrams (P&ID) and the logic control of the operating parameters. The procedure requires to identify the subsystem to analyse (node), pick a process parameter, as for example flow, temperature, pressure, pH and to study possible deviations from intentions by applying the “guide word”. More in details, the procedure for HAZOP analysis is to apply a number of guide word to various parts of the process design intention. This last tells what the process is expected to do. If the deviation is applicable, the possible causes, consequences are determined. These operations are repeated for each subsystem of the plant. Finally, a list of recommend action is suggested. It is possible to find the complete procedure in Crowl et al. 2011. HAZOP procedure if compared to other techniques (*i.e.* Checklist analysis) is more comprehensive and complete but also more time-consuming. HAZOP has a higher potential for revealing hidden weak points that can be further developed by other techniques as fault, event tree (FE and EE) and failure mode and effect analysis (FMEA).

The raw data used for the study have been developed within Life Bitmaps project by all partners: information on the process conditions (process flow diagrams and operating conditions) as well as information on the hardware including control system (P&ID) and operating manuals of the equipment are the basis for the application of the HAZOP safety analysis. The principal aim of the present study is to investigate the pilot plant from a point of view of safety and to check failure of the equipment design and control system. Following, the results for the first container has been reported. Part of the study derives from the experience performed on-site during the start up and running activity of the pilot plant. The first container of the pilot plant considered for the analysis is constituted by a neutralization reaction (N101) which is used to decrease the solution pH from 12 to 7, a storage tank (TK102), three identical bioreactors (R101, R012 and R103), which are used for the biodegradation of TMAH and finally the treated wastewater is sent to another tank located into the second container before being sent into the existing biological plant. The whole process is computer-controlled, starting from the neutralization of the initial wastewater and charging of the TK102 and fed in continuous mode the biological reactors. The inoculum phase of the reactors is performed at the initial phase of the

experimentally activity and it is manually carried out and therefore, this phase is considered one of the most dangerous, due to the fact that it is not automatic, and it will be considered separately from the rest of the analysis. The initial charging of the bioreactors consists of a transfer of active sludge through tanker; therefore the personnel carry out the operation in accordance to reference legislation (D. Lgs. 81/2008).

2.2 System limit and assumptions

The size of the equipment is properly dimensioned according to experimental data obtained at the laboratory scale, process analysis and scale up criteria, therefore it was assumed that the dimensions are sufficient for the process to perform properly. Equipment, piping, connections are clearly designed in according with good engineering practice. Moreover, the plant is operated and maintained in the manner envisaged by the design team. The system limits for the HAZOP analysis have been set, starting from the P&ID of a single functional units of the pilot plant as shown in Table 1. In this study, subsystem constituted by the thermostatic system is not included, anyway this system may be included in the further HAZOP studies with extended system limits or even a separate investigation of a particular subsystem may be adequate.

Table 1: Description of the subsystems analyzed by HAZOP

| NoSubsystem | Design intention | Medium |
|---|--|--|
| 1 Transfer system into N101 | Trasnsfer TMAH solution and sulfuric acid in N101 | Sulfuric acid line TMAH solution line |
| 2 Neutralization reactor | Neutralization of TMAH solution | Neutralized TMAH solution |
| 3 Transfer system N101-TK102 Storage TK102 | Transfer TMAH solution in TK102 Storage | Neutralized TMAH solution |
| 4 Transfer system Tk102-R101 | Transfer TMAH solution in R101 | Neutralized TMAH solution |
| 5 Biological reactor R101 | Degradation of TMAH | Culture liquid |
| 6 Transfer system R101-R02 | Transfer suspension (bacteria and TMAH solution) in R102 | Culture liquid |
| 7 Biological reactor R102 | Degradation of TMAH | Culture liquid |
| 8 Transfer system R102-R03 | Transfer suspension (bacteria and TMAH solution) in R103 | Culture liquid |
| 9 Biological reactor R103 | Degradation of TMAH | Culture liquid |
| 10 Transfer system R103 – tank storage | Transfer suspension (bacteria and TMAH solution) in R103 | Culture liquid |

3. Results and discussion

The raw data used for the study have been developed within Life Bitmaps project by all partners: information on the process conditions (process flow diagrams and operating conditions) as well as information on the hardware including control system (P&ID) and operating manuals of the equipment are the basis for the application of the HAZOP safety analysis.

The whole system has been divided into n. 10 subsystems and it has been assigned the design intentions for each subsystem that is the definition of what they have been designed for (see Table 1).

After the process information has been structure, a process flow diagram has been prepared as shown in Fig. 1 that describes the operations performed in each unit and the connection between them.

HAZOP safety analysis has been carried out for each unit including subsystem taking into account their design intentions. For the study of the transfer lines (subsystem No. 1, 3, 4, 6, 8, 10) the following parameters were considered: *flow, temperature, pressure, pH*; instead for process vessels (No. 2, 5, 7, 9) have been analyzed: *level, temperature, pressure, pH, oxygen concentration*.

The causes of failure have been classified to be technical or human nature, moreover another category has been added called “Other” in which causes relating, for example, to the external conditions have been grouped. For simplicity the consequences have been classified into three categories: “No process” consequence that makes the plant not working; “Release of materials”, consequence that potentially affects the safety of workers as the release of micro-organisms or TMAH effluent; “Off-specification”, consequence that causes any anomalies in the degradation process with possible damage of bacteria. It has been also considered whether identification of the occurrence of a consequence would be possible immediately or with delay. Each subsystem has been separately analyzed in order to identify in more detail possible system deviations. An overview of the results is reported in Figure 3.

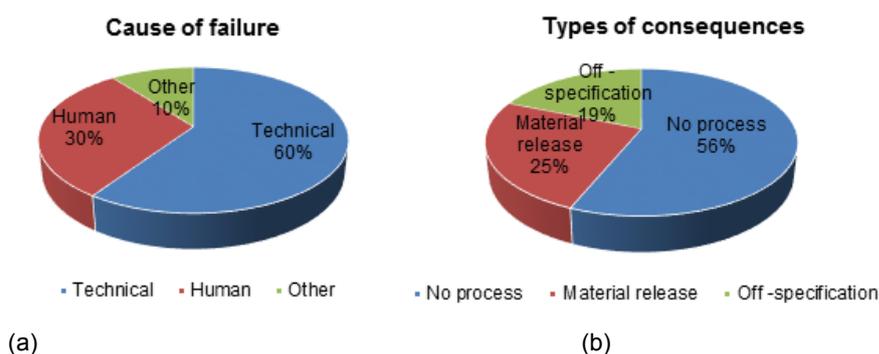


Figure 3: Cause of failure that could result in a deviation from the intention (a) and types of consequences resulting from anomalies from design intentions (b)

It is possible to observe that 60% of the causes identified in this study are of a technical nature (e.g. failure of pumps, valves, broken pipes and failure of the control system). Human error, as for example opening/closing of manual valves, accounts for 30%; instead external causes are 10% of the total.

The results (Figure 3b) show that the majority of consequences (56%) concerns process operability that provides for a stop of the wastewater treatment cycle. Regarding workers' safety, the release of material (mainly sulfuric acid, TMAH effluent or bacteria) is the major threat (25% of consequences). Moreover, from this analysis it was found that the possible causes related to the release of material are not immediately detectable for around 80% of the event (after inspection of the plant). This is an important consideration when assessing occupational safety and requires specific organizational measures and the use of personal protective equipment (PPE). The amount of material release as a consequence of a failure system or human error has not been, in this stage of the research activity, quantitatively estimated but it has been inferred that one third of the cases lead to a substantial release. Further the most demanding conditions (broken pipe or opening of sample valves) are those that interest the subsystems No 1-5. In the other subsystems the flowrate is low (around 25 L/h), it means that to have a large release of substance, the failure is not immediately identified. A possible release occurring in subsystems No.1-4 could cause a dispersion of TMAH effluent, or sulfuric acid, or neutralized TMAH effluent; instead for the subsystems No. 5-10 a dispersion of suspension containing TMAH, reaction intermediates and microorganism.

In according to specific literature, the health hazards of TMAH pentahydrate (solid) are very similar to those of the solution, however the solid is a GHS hazard category 3 for dermal acute toxicity, whereas the solution is a GHS hazard category 2 (higher hazard) for dermal acute toxicity. This difference in hazard category is likely due to the increased risk of dermal absorption of the chemical in solution (PennEHRS, 2020). In our case, TMAH is a solution hence with the following voice of toxicity: Acute toxicity, Oral (Category 2), H300; Acute toxicity, Dermal (Category 2), H310; Skin corrosion (Category 1), H314; Serious eye damage (Category 1), H318; Specific target organ toxicity - single exposure (Category 1), Central nervous system, H370; Specific target organ toxicity - repeated exposure, Dermal (Category 1), thymus gland, Liver, H372; Acute aquatic toxicity (Category 2), H401; Chronic aquatic toxicity (Category 2), H411.

Sulfuric acid (solution at 30%) Causes severe skin burns and eye damage H314; H318 - Causes serious eye damage H318; May cause cancer (Inhalation) 350; Harmful to aquatic life H402 (ChemTrade, 2020).

It is clear that for the safety of workers all appropriate PPE should be provided in order to reduce the exposure to toxic.

As regards the bacteria exposure, the workers could have biological risk due to aerosol formed as a consequence of the mixing and aeration system in R101, R102 and R103. The risk could be high considering that the plant is a confined space, anyway each unit of the pilot plant has the suction system and the reactors have the cap to reduce the aerosol dispersion. For a full-scale plant, the plant should be constructed in open-air, hence there is not the risk to have a specific zone with high concentration of aerosol; anyway, the biological risk will not be cancelled and safety precautions must be taken.

Safety management response may be grouped into three main categories: technical measures, maintenance practice and organization measures. From an analysis of the possible actions to prevent anomalies of the system, most of the measures required into operational procedures and should be incorporated into standard operating procedures (SOP), as maintenance and regular testing inspections. In this specific case, few technical interventions could be proposed, as installation of additional equipment or control system: this is because the plant even if in pilot scale has been designed and realized as a full -scale plant taking into account for safety aspects.

4. Conclusions

HAZOP methodology has been applied to investigate the potential risk for the industrial pilot plant wastewater treatment realized with Life bitmaps project (Grant Agreement N. LIFE 15 ENV/IT 000332). The plant treats three types of residual effluent coming from microelectronic industry, attention has been mainly focused on TMAH effluent treatment. TMAH is toxic and it is necessary to degrade and reduce its concentration below 0.4 mg/L to discharge into drainage system and to ensure 0.2 mg/L thresholds in water bodies. TMAH effluent was aerobically treated by activated sludge.

The pilot plant is almost completely automatic with automatic valves and other automatic systems to keep under control the operative conditions by remote control system. This minimizes operator input and hence the probability of human errors during the operations performed directly in the plant, that could have more harmful consequences. The analysis has been performed to point out the causes of failure, the consequences and the possible actions to identify and reduce the anomalies of the system. The results showed that the potential release of micro-organisms and the release of TMAH and inorganic acid (i.e. *sulfuric acid* used for the neutralization of the solutions) appears to be the most important issues to identify and control in order to reduce the harmful effects. The results also showed the possible precautions for avoiding hazardous deviations from the process, i.e. *operational procedures followed by equipment or design improvements, and maintenance practice*.

These actions will serve, mainly for the future upgrading at the full-scale plant, two purposes: they ensure (1) process and product safety (quality assurance) and (2) human and environmental safety.

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