

# Risk Assessment of Chemical Interactions in Wastewater Treatment: a Safety Engineering Approach

Astan Traoré<sup>a</sup>, Pierre Hodot<sup>b</sup>, Sabrina Guerin<sup>b</sup>, Sam Azimi<sup>b</sup>, Christophe Proust<sup>c</sup>, Edvina Lamy<sup>a,\*</sup>

<sup>a</sup> Alliance Sorbonne Université, Université de Technologie de Compiègne, EA 4297 TIMR (UTC/ESCOM), Centre de Recherche de Royallieu, - CS 60 319 - 60 203 Compiègne cedex, France

<sup>b</sup> Syndicat interdépartemental pour l'assainissement de l'agglomération parisienne SIAAP, 82 avenue Kléber 92700 Colombes, France

<sup>c</sup> Institut national de l'environnement industriel et des risques INERIS, av Parc Alata, 60550 Verneuil en Halatte, France  
[edvina.lamy@utc.fr](mailto:edvina.lamy@utc.fr)

Wastewater treatment plants (WWTPs) rely on various chemicals for essential processes such as sludge treatment, odour control and disinfection. However, the handling and storage of these chemicals present significant safety challenges, as incompatible substances can react to form hazardous, toxic, flammable or explosive compounds. This study focuses on the Seine Aval wastewater treatment plant (Service public de l'assainissement francilien, SIAAP, France), where large-scale chemical storage increases the potential risks associated with accidental mixing. A systematic risk assessment was conducted using Safety Data Sheets (SDS) to identify the physico-chemical properties of stored chemicals and determine possible hazardous reactions, including exothermic events, toxic gas releases and combined thermal and chemical hazards. The study aims to enhance process safety and loss prevention by developing a hazard classification tool that categorizes risks based on reagent compatibility. This approach provides a structured framework for improving chemical risk management, optimizing storage and handling protocols, and ensuring safer operations in WWTPs.

## 1. Introduction

Wastewater treatment plants (WWTPs) are critical infrastructures that ensure environmental protection by processing domestic, industrial and stormwater effluents. However, these facilities also present significant process safety and risk management challenges, particularly due to the storage and handling of hazardous chemicals and the generation of biogas. The Syndicat Interdépartemental pour l'Assainissement de l'Agglomération Parisienne (SIAAP) is responsible for the treatment of wastewater in the Paris region. Operating six wastewater treatment plants, SIAAP processes approximately 2.5 million cubic meters of wastewater per day, serving over 9 million residents across a service area of 1,800 km<sup>2</sup>. The wastewater, which includes domestic, industrial and stormwater effluents, is collected through a vast 440 km sewer network and transported to one of the six treatment plants. The Seine Aval wastewater treatment plant (SIAAP, France), one of the largest in Europe, treats approximately 1.5 million cubic meters of wastewater per day and has been classified as a Seveso site since 2010 due to the presence of large quantities of biogas and high-risk chemicals.

It is well known that biogas production at WWTPs introduces explosion, fire and toxic hazards, but the operators are much less aware that improper mixing of chemicals in such plant may be very hazardous also, with similar consequences. The ARIA database (Analysis, Research and Information on Accidents), which provides feedback from over 54,000 accidents and incidents occurring in France or abroad, highlights that most technical incidents in WWTPs are linked to biogas leaks (ARIA 59817, 47989, 53089, 44662...), but chemical accidents are also present. At Seine Aval, large volumes of methanol and ferric chloride are stored, both of which are classified as high-risk substances (Lewis and Sax, 1987). Ferric chloride, in particular, has been involved in multiple chemical incompatibility incidents, reacting violently with strong bases such as sodium hypochlorite

(ARIA 44835, 43664, 47623, 18064, 17351), sodium chlorite (ARIA 15598), sulfuric acid (ARIA 30614) and sodium hydroxide. Most of these incidents result from human error during unloading of one of the two products, which mix and form a toxic cloud, notably chlorinated vapours (Pasquet V., 2020) leading to poisoning of varying severity depending on the level of exposure.

Given the potential severity of these risks and because many aspects are unknown, this study focuses on process safety and loss prevention strategies to mitigate chemical incompatibility hazards in WWTPs. By analysing accidental chemical reactions and historical incidents, this study aims to develop a structured hazard classification tool to support risk assessment, storage optimization and safer handling of chemical reagents. At this stage, this work is restricted to clarification of chemical incompatibility situations and find easy ways to identify hazards on site. The work on consequence prediction and control measures is actually a subject for ongoing research.

## 2. The chemical incompatibility hazard for SIAAP

The identification of chemical incompatibilities and the associated hazardous reactions is a critical aspect of ensuring process safety and loss prevention in wastewater treatment plants. A number of tools are available and can provide further insights to understand the incompatibility phenomenon. The Chemical Reactivity Worksheet tool (CRW), initially developed in 1995 by Dr. James Farr from the National Oceanic and Atmospheric Administration (NOAA), is a free software tool widely used in industry to assess the compatibility of various chemicals. It can help to identify potential chemical hazards that may occur when different chemicals are mixed. A product from the CAMEO (Computer-Aided Management of Emergency Operations) software suite, CAMEO chemicals is also a useful tool for chemical reactivity predictions. However, both tools are optimized for binary mixtures and do not explicitly predict incompatibility for multiple chemicals simultaneously. Therefore, they may struggle to accurately predict hazards associated with reactions that occur under specific conditions (temperature, pressure, humidity) or when specific impurities are present in the incompatible mixture.

The typology of accidents due to incompatibilities results from the identification of the chemicals used in the process, the study of their reactivity when mixed with other species and the analysis of feedback. The chemicals used in large quantities in the wastewater treatment processes at the Seine Aval plant were identified and the reactivity of these chemicals when mixed with others was studied by consulting their Safety Data Sheets (SDS) and reviewing relevant scientific literature. This allowed for the development of a chemical incompatibility matrix, which outlines the potential risks associated with accidental chemical mixing. The study focused on 21 chemicals present in quantities greater than 1 m<sup>3</sup>, as such quantity can produce consequences outside the plant. (Table 1). These chemicals were selected due to their common use in SIAAP's wastewater treatment processes and their potential for hazardous interactions.

*Table 1: List of chemicals present in proportions greater than 1 m<sup>3</sup>*

List of 21 chemicals inventoried on the sites		
Ferric Chloride	Fuel oil	Alufer
Sodium Bisulfite	Methanol	Propane
Sodium hydroxide	Acetylene	Citric Acid
Sodium Thiosulfate	Slaked Lime	Formic Acid
Sodium Bicarbonate	Calcium Oxide	Sulfuric Acid
Sodium Hypochlorite	Calcium Nitrate	Phosphoric Acid
Ammonium Hydroxide	Hydrogen Peroxide	Hydrochloric Acid

By analyzing these chemicals and their reactivity profiles, a literature search was first carried out to identify potential hazardous reactions that can occur when incompatible substances are mixed or when a chemical reacts with its container. Hydrogen peroxide is known to pose fire and explosion hazards, the risk of explosion is heightened by factors such as temperature, concentration and the presence of catalysts or impurities (Wu et al., 2010). Strong oxidizing acids also pose a risk, since they can react violently with other acids, leading to explosions, toxic gas release, or extreme heat generation. For instance, the combination of nitric acid (HNO<sub>3</sub>) with formic acid (CH<sub>2</sub>O<sub>2</sub>) has been reported to produce acid gases and significant heat, potentially resulting in explosive reactions (Huang et al., 2013). The scientific literature (Margossian, 2010) underlines that the reaction between an acid and certain compound such as hypochlorite, cyanides and sulfites can lead to the formation of a dangerous gas causing intoxication. In the specific context of the SIAAP plant, a problematic scenario could be the reaction between sodium bisulfite and hydrochloric acid, which produces gaseous sulfur dioxide (SO<sub>2</sub>), or the reaction between hydrochloric acid and sodium hypochlorite, which produces gaseous chloride (Cl<sub>2</sub>).

These toxic gases, even in low concentrations, can be dangerous to human's health. So, in the event of toxic gas formation, the risk created could be significant.

Among hazardous chemical interactions, acid-base reactions are a concern, particularly those involving strong acids and bases, as they are often exothermic. Depending on the concentration of the acids/bases involved, the reaction can result in the vaporization of an aerosol containing a toxic product.

Additionally, the potential for flammable gas formation was identified, particularly in redox reactions that could lead to the release of hydrogen gas (H<sub>2</sub>). These reactions often occur in factories. In fact, products such as strong acids can rapidly attack storage tanks. These products, known as reducers, mainly oxidize reactive metals (such as iron, magnesium or zinc). Available feedback (ARIA 169, 22278, 31082) reports several explosions occurred after the accidental ignition of hydrogen gas (H<sub>2</sub>) produced by the attack of a steel tank by its container, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). In fact, if the leaked hydrogen is not ignited immediately and instead fully mixes with air to form a combustible hydrogen-air mixture, ignition can lead to deflagration (Hu et al., 2023), which may escalate into detonation. However, compared with a toxic cloud, to create a significant risk, a suitable concentration and ignition sources (such as static electricity, open flame, hot surface...) are required and can sometimes be generated by maintenance operation performed close to the reservoir in concerned, as reported by Sales et al. (2007) and in the (ARIA 22278) accident feedback.

Another risk involves exothermic reactions created by the dissolution of one product in another. The most classic case is the dissolution of concentrated sulfuric acid in water. This type of reaction can be exothermic and therefore create a risk for SIAAP plants. Since the final goal is to mitigate the chemical incompatibility danger, the risk needs to be described accurately. The focal point is that the accident that may occur for which the causes need to be identified (circumstances, nature of the incompatibility, quantities, ...) and the consequences calculated. Starting from this point, the risk could then be ranked and mitigation strategies defined. Thus, from the preceding information and some brainstorming, the following typology of accidents was defined for SIAAP:

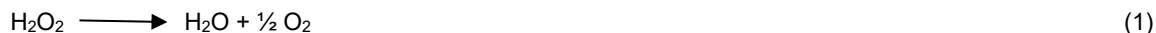
- A. Formation of an unstable substance that explodes (e.g. mixture of a peroxide and a combustible).
- B. Formation of a toxic cloud (e.g. release of Cl<sub>2</sub> from a NaOCl+acid mixture)
- C. Formation of an aerosol containing a toxic reagent by vaporization of water (e.g. dissolution of concentrated sulfuric acid in water).
- D. Formation of a flammable cloud (e.g. release of H<sub>2</sub> by acid attack on a metal)
- E. Thermal degradation of equipment under the effect of excessive heating (e.g. plastic joints/tubes if temperature >80 to 100 °C following an exothermic reaction)
- F. Chemical degradation of equipment and corrosion (e.g. attack on metal container by acid content)
- G. Plugging due to solid formation (e.g. precipitation reactions)

Each type of accident was analyzed starting from the chemical dimension, looking for some identification parameters and for potential quantities of hazardous substances. The human and organizational aspects will be subject for further research.

### 3. Identification of relevant physico-chemical parameters

#### 3.1 Scenario A\_ Formation of an unstable, exploding substance

Unstable substances typically contain both a powerful oxidant and a combustible. The reaction can be highly exothermic, leading to rapid energy release that may result in an explosion under certain conditions, such as impact or temperature increases. In the context of SIAAP operations, hydrogen peroxide is a potential oxidant. When mixed with certain products, it can decompose in a highly exothermic reaction, as shown in Eq(1):



The decomposition of hydrogen peroxide releases oxygen, which can trigger secondary combustion reactions. At SIAAP, methanol is unlikely to be accidentally mixed with hydrogen peroxide, since they are used at distinct sites. However, fuel oil, sometimes used by SIAAP subcontractors, could be a concern. To estimate the effects of hydrogen peroxide decomposition, the reaction is assumed to be complete in a worst-case scenario. Hess's Law can be used to calculate the enthalpy change of the decomposition reaction Eq(2). Based on these parameters, the reaction releases 98 kJ of heat per mole of hydrogen peroxide. Depending on initial hydrogen peroxide concentration, the released energy could significantly raise temperatures, potentially vaporizing water and causing explosive pressure effects similar to the detonation of explosives. The hydrocarbons and alcohols mentioned above are easily vaporized and ignited under these conditions. This situation would pose a significant safety risk, with a potential for catastrophic consequences.

$$\Delta H_{\text{réaction}} = \frac{1}{2} \cdot \Delta H_{\text{O}_2} + \Delta H_{\text{H}_2\text{O}} - \Delta H_{\text{H}_2\text{O}_2} = 0 + (-285.8) - (-187.8) = -98 \text{ kJ/mol} \quad (2)$$

To characterize this scenario, it is sufficient to identify the “peroxide” and “combustible” properties, which are usually clearly accessible on the safety data sheet.

### 3.2 Scenario B\_ Formation of a toxic cloud

A leak of a toxic substance (chlorine, ammonia, phosgene, acid, etc.) from a plant can cause serious damage through inhalation, skin or eye contact, or ingestion. The effects may include acute lung oedema, nervous system damage or chemical burns to the skin or eyes. Emissions of toxic substances in SIAAP operations, could result from the degradation of chlorinated substances (ferric chloride, sodium hypochlorite, hydrochloric acid), releasing chlorine Cl<sub>2</sub> gas, or sulfurous substances (sulfuric acid, sodium bisulfite), releasing sulfur dioxide SO<sub>2</sub> gas. Typically, these toxic gas emissions result from aggressive chemical reactions, since the compounds in question are relatively stable. These reactions include acid-base neutralization and oxidation-reduction. In order to consider the release of one of these toxic substances, it seems essential that the pairing can be described as acidic and basic, or oxidizing and reducing. For example, the mixture of sodium hypochlorite and hydrochloric acid can release Cl<sub>2</sub> gas. This is also the case for FeCl<sub>3</sub> with concentrated sulfuric acid (which acts as an oxidizer) for a reaction at high temperature or in the presence of a reducing agent. To characterize this scenario, it is necessary to identify the “oxidizing” and “reducing” or “acidic” and “basic” properties of the product pair, and also identify the presence of Cl (chlorine) and S (sulfur) in the molecules. This information is usually available on safety data sheets.

### 3.3 Scenario C\_ Formation of an aerosol containing a toxic reagent by water vaporization, and scenario E\_ Thermal degradation of equipment

These scenarios involve the same reactions. It is only the temperature levels reached that differ. The specific case of reactions of non-combustible products with hydrogen peroxide has been identified. Many substances can induce the decomposition of hydrogen peroxide depending on its concentration. At the present stage of method development, it might be appropriate to consider that all products other than those declared compatible on safety data sheets are incompatible and induce decomposition and heat release. Acid-base reactions in aqueous media generally generate heat through the reconstitution of water molecules based on the neutralization of hydroxide and hydronium ions. The exothermicity of the reaction is therefore highly dependent on the relative concentrations of these ions, and the criteria to be adopted for this scenario are examined below. They focus on the Ni/m molar concentration of the ion, OH<sup>-</sup> or H<sup>+</sup>, deficient in the neutralization reaction, which enables the targeted critical temperature (T<sub>critical</sub>) to be released by neutralization.

$$Ni * 60000 = 2 * m * C_p * (T_{critical} - T_{ambient}) \quad (3)$$

Where Ni is the number of moles of the deficit ion, C<sub>p</sub> is the heat capacity of the final mixture, similar to that of water (4000 J/(kg.°C) can be assumed), and (2 \* m) is the mass of the initial mixture (identical mass of base and acid are assumed). Finally:

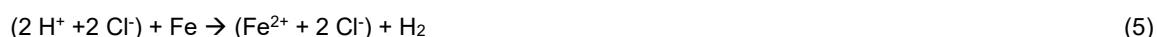
$$\frac{Ni}{m} = \frac{8000 * (T_{critical} - T_{ambient})}{60000} \quad (4)$$

For T<sub>critical</sub> = 100 °C and T<sub>ambient</sub> = 20 °C, Ni/m = 11 and for T<sub>critical</sub> = 80 °C and T<sub>ambient</sub> = 20 °C, Ni/m = 8.

To assess the heating induced by an acid-base neutralization reaction, there does not seem to be a criterion directly accessible from the safety data sheet: consider the solvation reaction of the acid (or base) and estimate the quantity of hydronium (or hydroxide) ion per unit mass. If the values exceed the above thresholds, there is a possibility of scenarios C or E occurring.

### 3.4 Scenario D\_ Formation of a flammable cloud

The most likely situation is an acid attack on metals or reducing materials, resulting in the release of hydrogen. When metals come into contact with acidic substances, they undergo chemical reactions that lead to surface deterioration. Acids release H<sup>+</sup> ions. H<sup>+</sup> ions can oxidize (take electrons from) metals, particularly those that are more reactive, such as zinc, iron, aluminum, etc. typically metals at the top of the metal reactivity range. This process is especially significant in industrial settings, where different alloys face corrosion challenges in acidic environments. For example, for iron, the reaction involved is:



However, these corrosion reactions are heterogeneous, meaning that the different phases involved (solid metal, acid in solution, reaction products) are not in the same phase (solid, liquid, gas). This has a direct impact on the speed and scale of the reactions, as well as on the quantity of gas produced. Reactions are therefore slow and produce small volumes of flammable gas.

### 3.5 Scenario F\_ Accelerated chemical degradation of equipment/container attack

Acids react with certain metals to form hydrogen, attacking the metal in a corrosion reaction. Concrete appears to be relatively insensitive to corrosion. Plastics can be sensitive to solvents. The incompatibility criteria corresponding to this scenario can be established as follows:

- Acids can accelerate the degradation of light metals with a molecular weight lower than that of zinc.
- Solvents (such as hydrocarbons and alcohols) can lead to hazardous reactions with the double bonds in plastics like ABS and polybutadiene.

In SIAAP, this scenario is relevant when acids come into contact with metals or when solvents interact with plastic containers. The critical physico-chemical parameters for this scenario include the material composition of equipment and the chemical reactivity of the substances involved.

### 3.6 Scenario G\_ Clogging by solid formation

This situation typically corresponds to the formation of precipitates and concerns all salts resulting from acid-base reactions and corrosion. This may be a point of vigilance to be associated with scenarios C, E and F.

Consequently, the physico-chemical parameters to be extracted from the product data sheets are:

- Peroxide character
- Flammability
- Oxidizing or reducing properties
- Contains chlorine or sulphur (possibly bromine or fluorine)
- Acidic or basic character
- Hydronium/hydroxide ion concentration greater than 11 mol/kg
- Hydronium/hydroxide ion concentration greater than 8 mol/kg
- Metal lighter than zinc
- Plastics containing double bonds

## 4. Toward a decision tool

### 4.1 Chemical hazard classification tool

To demonstrate the effectiveness of the methodology developed, ferric chloride (diluted to 40%) is used as a case study, as it is a commonly used reagent at SIAAP. Key properties of interest include the substance's potential for peroxide formation, combustibility, presence of halogen elements (F, Cl, I, Br, S), acid/base characteristics, oxidation/reduction behaviour and its interactions with materials such as light metals and plastics containing double bonds. According to its safety data sheet, ferric chloride is an acidic substance that can produce three hydronium ions per  $\text{FeCl}_3$  molecule, resulting in a theoretical Ni/m ratio of 7.4, a threshold value for potential safety hazards.

Based on this, the matrix highlights the following safety scenarios for ferric chloride under specific conditions:

- Scenario B: Interaction with a base could lead to the formation of a toxic cloud.
- Scenario D: Contact with a light metal may lead to the formation of hydrogen gas, creating a flammable cloud.
- Scenario F: The degradation of equipment and containers may be accelerated through corrosion reactions with acids.
- Scenario G: Solid formation, resulting from acid-base reactions, could lead to clogging and operational disruptions.

### 4.2 Establishment of a criticality grid

This study proposes a method to rank accident scenarios according to their impact. A criticality grid is used to categorize scenarios into three levels: low, moderate, and high criticality. The classification is based on three key criteria: the extent of the effects, severity, and accident kinetics.

- Extent of effects: Scenarios are classified as impacting the unit (localized), the plant, or beyond the plant boundaries.
- Severity: Assessed based on health and structural damage thresholds, ranging from minor material damage to significant external fatalities.
- Accident kinetics: Evaluates the speed of development, affecting the feasibility of sheltering and intervention.

To establish the criticality of a scenario, the level corresponding to the most 'critical' criterion was selected. Ultimately, the rating presented in Table 2 was obtained.

Table 2: Assessment of event criticality

Scenario	Severity	Extent of effects	Kinetics	Criticality
A	Death and destruction	The plant	Seconds	High
B	Intoxication	Beyond the plant	Minutes	High
C	Intoxication	The unit	Minutes	Moderate
D	Injury and destruction	The unit	Seconds	High
E	Equipment degradation	The unit	Minutes	Moderate
F	Equipment degradation	The unit	hours	Low
G	Operational disruptions	The unit	hours	Low

### 4.3 Prevention strategies and existing control measures at SIAAP

Chemical risk prevention involves the separate storage of incompatible substances in appropriate containers to prevent dangerous reactions. To avoid inadvertent mixing during product delivery and unloading on the site, the Seine Aval WWTP employs an IDIS pot (Installation de Dépotage Intrinsèquement Sûre) to ensure that the product received is indeed the one expected, thus preventing incompatible mixing within the storage tank.

## 5. Conclusions

The work analysis performed in this paper lead to the creation of an "incompatibility matrix" that serves as a tool for identifying potential risks when a new product is introduced into the process. This matrix, represented as a diagram, was designed to identify potential incompatibilities between the newly-introduced product (substance or material) and the existing substances or materials in use. This tool may evaluate the safety risks associated with new additions in a systematic manner, considering factors such as chemical reactions, energy release, and material degradation. SIAAP's accident history confirmed that these scenarios are plausible and should be carefully monitored. Beyond the screening that the tool allows, which has to be validated and refined, the intention is to accurately estimate the consequences of each scenario (quantity, dispersion, speed), identify the causes of these incompatible mixtures and then propose safety measures to mitigate them. Tests are planned for the chemical aspects, while a risk analysis method should be chosen, that can integrate the socio-technical aspects for probability estimation. For this purpose, the precise course of a few accidents will be analyzed as a starting point.

## References

- ARIA database, the reference for feedback on technological accidents <[www.aria.developpement-durable.gouv.fr/le-barpi/la-base-de-donnees-aria/](http://www.aria.developpement-durable.gouv.fr/le-barpi/la-base-de-donnees-aria/)> accessed 20.01.2025
- Farr J. K., Gorman D. B., Sliva D., Hielscher A., Nguyen T., Baran G., Drake B. L., Ford E., Frurip D., Mulligan K., Ryan J. W., Viveros, D., 2017, Expanded Chemical Reactivity Worksheet (CRW4) for determining chemical compatibility, past, present, and future. *Process Safety Progress*
- Hu Q., Zhang X., Hao H., 2023, A review of hydrogen-air cloud explosions: The fundamentals, overpressure prediction methods, and influencing factors, *International Journal of Hydrogen Energy*, Volume 48, Issue 36,
- Huang Y.H., Chiang C.C., I Y.P., Kuo C.T., Wu S.H., Hsu J.P., Charpentier J.C., 2013, Incompatible reaction evaluation and accident investigation of various acids in chemical industries. *J Therm Anal Calorim* 114
- Lewis R.J., Sax N.I., 1987, Hazardous chemicals desk reference. Van Nostrand Reinhold Company Inc. Library of congress Catalog Card Number 87-2084 ISBN 0-442-28208-7
- Margossian N., 2010, Treating chemical risk, risk and hazard science, LAVOISIER, Paris, France (in French)
- Miletiev R., Simeonov I., Stefanova V., Georgiev M., 2013, Thermodynamic analysis of the hydrogen peroxide decomposition parameters. *J Therm Anal Calorim* 113, 985–989
- Pasquet V., 2020, Ferric chloride: a corrosive liquid for everyday use. Faced with the risk, feedback, 565, pp.10-12. (hal-03019017) (in French)
- Pohanish R.P., Greene S.A., 2009, Wiley guide to chemical incompatibilities. John Wiley & Sons, Inc., Hoboken, New Jersey.
- Sales J., Mushtaq F., Christou M.D., Nomen R., 2007, Study of Major Accidents Involving Chemical Reactive Substances: Analysis and Lessons Learned, *Process Safety and Environmental Protection*, Volume 85
- Wu, M.L., Tsai, W.-J., Ger, J., Deng, J.F., 2003, Clinical experience of acute ferric chloride poisoning. *Veterinary and Human Toxicology*, 45(5), 243–246
- Wu S.H., Chi J.H., Huang C.C., Lin N.K., Peng J.J., Shu C.M., 2010, Thermal hazard analyses and incompatible reaction evaluation of hydrogen peroxide by DSC. *J Therm Anal Calorim* 102, 563–568