# Pollution prevention in food industries through both cleaning of closed equipment with ozonated water and cleaning in place (CIP) systems

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## Abstract

Cleaning and disinfection are key operations in the food industry for safety reasons but produce a significant environmental impact in terms of water use and wastewaters as stated in the Reference Document on Best Available Techniques in the Food, Drink and Milk industries. Care areas rely on a range of chemicals such as chlorine, quaternary ammonium compounds, etc. Health and environmental concerns are supporting the need for alternative sanitation technologies. The data shown here is part of a LIFE project that aims to reduce the environmental impact of cleaning operations through the use of ozone, as it is a very strong oxidant and a wide spectrum antimicrobial agent with potential environmental benefits over other sanitizers. An analysis of the different factors involved in an ozone based CIP system is considered, comments in relation to Best Available Technologies concerning cleaning and disinfection are presented, environmental data related to in-process operations obtained in the collaborating industries of the winery and dairy sectors is shown and a pilot plant designed to perform comparative demonstration trials is described. The expected results of ongoing tasks are environmental indicators on water and energy consumption, wastewater quality and the cleaning and disinfection efficiency of ozone based cleaning versus conventional cleaning.

*Keywords: CIP, wastewaters, ozone, food industry.*

WIT Transactions on Ecology and the Environment, Vol 111, 
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/WP080601

# 1 Introduction

The need to keep high hygienic standards is a main concern in the food industry. Most care areas rely on a range of chemicals to maintain an acceptable hygiene regime such as chlorine, quaternary ammonium compounds and others. However, this leads to significant environmental considerations as frequent cleaning is required and water is used intensively along with chemicals. Some of the most important cleaning tasks are those related to the washing of process vessels, storage tanks and pipes where cleaning in place systems (CIPs) are of common use. CIPs are characterized by automatic cleaning programs based on a succession of several solutions of water, cleaning chemicals and disinfection agents that are discharged into sewer systems together with large amounts of water necessary to rinse out residual chemicals. Also, cleaning wastewaters contain organic material from product remnants and removed deposit soil. When chlorine based compounds combine with organic residues the results could potentially be extremely harmful to people. So health and environmental concerns with chemical use on food products or food contact facilities are supporting the need for alternative sanitation technologies. In this sense, the potential utility of ozone lies in the fact that ozone is a stronger oxidant than chlorine and it has been shown to be effective over a wider spectrum of micro organisms. But, unlike other disinfectants, it leaves no chemical residuals and degrades to molecular oxygen upon reaction or natural degradation. The most researched and developed food industry applications of ozone are those in which the ozone is applied directly to the food to disinfect it. A large number of studies have demonstrated its efficiency in all types of products and in a wide range of operations (raw materials, cleaning and disinfection, product cooling water treatment and food conservation and storage, among others) [1]. Different studies reported show that cleaning using ozone as disinfecting agent is efficient [2–5] and might improve the environmental performance of cleaning operations in terms of reduction of the amount of water needed for cleaning of vessels and surfaces compared with conventional systems [6–9]. Overall chemical costs are reduced, sewage disposal costs are reduced and overall system deterioration is reduced when using ozone-enriched water rather than hot water or traditional anti-microbial chemicals [10]. Regarding environmental data related to cleaning operations the Reference Document on Best Available Techniques in the Food, Drink and Milk Industries (FDM BREF) [11] admits that strong information imbalances and gaps exist. In general, at the BREF, the current consumption and emission level data provided were not linked with process descriptions, operating conditions, installation capacity, and sampling and analytical methods. Most of the work already reported on the use of ozone for sanitizing purposes focus on its disinfecting capacity but scarce data on its environmental benefits has been obtained. The reduced environmental impact is a significant factor that may favour the future development of ozone in all countries, especially in Europe. Thus, Directive 96/61/EC concerning Integrated Pollution Prevention and Control (IPPC) could indirectly encourage ozone use in EU countries, if ozone based cleaning and disinfection was considered a BAT.

# 2 Methods

The project aims to demonstrate the environmental benefits of ozone water for cleaning and disinfection of closed equipment compared to other conventional agents. The work focuses on winery, dairy and brewery sectors as representative of industries where large amounts of water is consumed and discharged as a consequence of cleaning and disinfection of closed equipment. The methodology consists on the following tasks:

- Preliminary actions: in order to get the necessary multidisciplinary background different specific studies and state of the art reviews were produced on Best Available Technologies (BATs) Documents, cleaning in place (CIP) technology and Ozonation Technology. At the same time, field work was performed in collaborating companies in order to obtain a better knowledge of current practices at industrial scale and get environmental impact data of in-process operations by sampling and characterisation of cleaning wastewaters.
- Ozone CIP prototype design and construction. Considering all the important input data from the former action, a pilot plant was designed and constructed that allows for the simulation of conventional CIP protocols and running ozone based protocols, so comparative indicators of the environmental impact may be obtained.
- Demonstration activities: consisting on the design and execution of the comparative trials.
- Evaluation of results: in terms of water, energy and chemical consumption, wastewater generation, and hygienic efficiency.

# 3 Results and discussion

## 3.1 Environmental diagnosis of current cleaning operations of tanks in cellars and dairies

In general, at the FDM-BREF, the current consumption and emission level data provided were not linked with process descriptions, operating conditions, installation capacity, sampling and analytical methods and statistical presentations. Different amount of process and environmental information is already available for brewery, winery and dairy sub-sectors. Through the visits to facilities and interviews with technicians of the three sub-sectors we have observed that the winery sub-sector is formed by a bigger number of small sized companies than the dairy sector, and that the brewery sector is formed just by big-sized companies. The dramatic lack of existing data in the winery sector, and the relatively homogeneity in the operations carried out at any brewery led us to focus efforts on getting environmental in-process information at industrial level in wineries and dairies. Brewery sector data may be consulted at the FDM BREF and at the Guía de Mejores Técnicas disponibles en España del Sector Cervecero (2005), so no further comments will be brought here on this sector.

### 3.1.1 Environmental data related to cleaning and disinfection of tanks in wine cellars

The BREF states that almost all the water consumed in a winery is used for cleaning purposes; nevertheless, no reference data on consumption is given in relation to production capacity neither data on particular consumption for cleaning purposes. Table 1 shows data collected by ainia in relation to overall consumption of water in relation to production capacity. Assuming that almost all water consumed is used for cleaning operations, wastewater ratios would be similar.

Table 1: Water consumption in wineries.

| | |
|---|---|
| Wine elaborator (m3 water consumed/m3 wine produced) | 0.09-0.37 |
| Wine bottler (m3 water consumed/m3 wine bottled) | 0.35-1.23 |

Table 2: Wine parameters.

| | pH | Cond (mS/cm) | COD (mg/L) | N (mg/L) | PO4-P (mg/L) |
|---|---|---|---|---|---|
| Red wine | 3.41 | 2.10 | 171,000 | 580 | 90 |
| Rose wine | 3.43 | 2.31 | 176,000 | 520 | 100 |
| White wine | 3.62 | 2.34 | 183,500 | 520 | 90 |

Table 3: Untreated effluent in wineries.

| Parameter | Elaborator | Bottler |
|---|---|---|
| pH | 4.06 -8.01 | 7.21 – 8.14 |
| Conductivity (μS/cm) | 429 – 5,090 | 525 – 2,000 |
| SS (mg/l) | 10 – 948 | 46 – 104 |
| BOD5 (mg O2/l) | 36 – 16,296 | 20 – 782 |
| COD (mg O2/l) | 76 -30,750 | 32 – 1,245 |
| Pt (mg P/l) | 2.2 – 82 | <1 – 3.6 |
| NKT (mg N/l) | 2 - 53 | 7 – 66 |
| toxicity | 0 - 250 | 0 – 30 |

The highest concentrated wastewater is produced during fermentation, fining and ageing/racking due to the washing out of the sediments. If solids are not separated, the waste water is highly contaminated. Even after the recovery process, the wastewater shows an acidic character except when caustic solutions are used in the elimination of tartrates or during the conditioning of bottles. We have analysed samples of wine in order to know the level of organic load transferred to the cleaning waste waters as a consequence of product remnants in (table 2). Also, a range values for global wastewaters of wine elaborators and wine bottlers have been obtained (table 3). The wide ranges obtained show the influence of performing a proper segregation of remnants. Different cleaning patterns have been monitored (table 4): manual pressure cleaning and cleaning with spray ball, cleaning with or without recovery of initial rinse (i.e. with fewer

Table 4: Cleaning wastewaters in wineries.

| Stage | Characteristics of cleaning wastewaters in wineries | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **A** | | | **B** | | | **C** | | | **D** | | |
| | pH | cond | COD | pH | cond | COD | pH | cond | COD | pH | cond | COD |
| Rinse with water | 4-7 | 500-1,500 | 5,000-20,000 | For alcohol recovery | | | For alcohol recovery | | | like case A | | |
| Alkaline washing | no | | | no | | | Reused and tartrate recovery | | | no | | |
| Disinfection | no | | | no | | | no | | | 5-8 | 1100-2700 | 600-1,100 |
| Rinsing with water | no | | | 4-7 | 800-1,500 | 135-2,600 | >10 | >20,000 | 110 | 6-8 | 1,100-2,600 | 10-150 |

No = step not performed.

remnants), cleaning after alkali wash and some more complex protocols. These results will show an idea of the impact produced by particular cleaning operations as manual operation is common practice and the amount of water employed in rinsing is very dependant on the operator doing the job.

### 3.1.2 Environmental data linked to the cleaning and disinfection of close equipment in the dairy sector

Water consumption in dairies is mainly associated with cleaning operations. The following table shows some general ratios on water consumption in dairy industries:

Table 5: Water consumption in European dairies (European Dairy Association, [12], assumed as reference for the FDM BREF [11] (page 186)).

| Product | Water consumption(*) (l/kg processed milk) | |
|---|---|---|
| | MIN | MAX |
| Market milk and yoghurt | 0.8 | 25 |
| Cheese and whey | 1.0 | 60 |
| Milk powder. Cheese and/or liquid products | 1.2 | 60 |

(*) Cooling water is included.

The FDM BREF states that waste water is the main environmental issue in the dairy sector. The largest proportion of waste water is cleaning water. This has been observed in the visited industries where water consumed is used in a percentage higher than 80% for these purposes. Loss of products by spillage is of great importance because of the extreme organic load transferred to the wastewaters as can be seen in table 7. Table 8 shows typical characteristics of untreated waste waters from dairy industries obtained from Environment Agency of England and Wales, 2000 and assumed by the FDM BREF 2006 as reference range values. Regarding to particular cleaning operation table 9 shows the data obtained by ainia through sampling in different dairy companies. The data relates to conventional cleaning and disinfection protocols of different closed equipment used in collaborating companies, mainly milk storage tanks but also, curd vats, yogurt fermentation tank and pasteurizer of milk cleaning have been considered.

Table 6: Milk and yogurt samples (ainia).

| | pH | Conductivity (mS/cm) | COD (mg/L) | N (mg/L) | PO4-P (mg/L) |
|---|---|---|---|---|---|
| Milk | 6.66 | 5.25 | 160,500 | 590 | 1,680 |
| Yogurt | 4.15 | 155 | 184,500 | 370 | 980 |

Table 7: Untreated dairy wastewaters.

| Component | Range |
|---|---|
| SS | 24-5,700 mg/l |
| TSS | 135-8,500 mg/l |
| COD | 500-4,500 mg/l |
| $BOD_5$ | 450-4,790 mg/l |
| Fats | 35 - 500 mg/l |
| Ammonia-N | 10 - 100 mg/l |
| Nitrogen | 15 - 180 mg/l |
| Phosphorous | 20 - 250 mg/l |
| Chloride | 48 - 469 mg/l |
| pH | 5.3- 9.4 |
| Temperature | 12 - 40 ºC |

Table 8: Cleaning wastewaters in dairies.

| | pH (ud) | Conductivity (µS/cm) | COD (mg $O_2$/L) |
|---|---|---|---|
| Rinse with water | 8.1 – 11.61 | 430 – 1,700 | 28 – 1,465 |
| Alkaline wash | 12.8 – 13.11 | 13,280 – 39,200 | 196 - 568 |
| Rinse with water | 8.63 – 13.22 | 485 – 18,760 | 32 – 1,190 |
| Acid wash | 2.49 – 2.50 | 4,840 – 9,920 | 428 -958 |
| Rinse with water | 2.65 – 4.97 | 1,170 – 6,940 | 31 - 428 |
| Final rinse | 7.00-8.00 | 412 – 1,040 | 30 - 60 |

### 3.2 Integration of ozone technologies and CIP technologies: factors to consider

The objective of cleaning and sanitizing food contact surfaces is to remove food soils and films which bacteria need to grow, and to kill those bacteria which are present. CIP is used to clean interior surfaces of tanks and pipelines. The majority of cleaning and sterilizing liquids used in CIP systems are alkali or acid based and the system will allow accurate dosing of the concentrated cleaning agent to give a low strength solution suitable for cleaning process plant. A cleaning program can be composed of some of the following steps: (1) Pre-rinsing: Soiled equipment surfaces are rinsed with water to remove the gross amounts of loose food soils; (2) Cleaning Cycle: removal of residual food soils from equipment surfaces. This cycle may include: (a) Caustic wash, (b) intermediate rinse, (c) acid wash, (d) rinse with water; (3) Disinfection: all equipment surfaces are rinsed or flooded with a sanitizing agent; (4) Rinsing of all surfaces with water to thoroughly remove all remaining chemical solution. The cleaning solutions and operating conditions will depend on the nature of the soils to be removed, also, a variety of chemicals are available for the sanitizing step. In the field of cleaning and disinfection, the potential applicability of ozone is based on the fact that ozone is stronger oxidant than chlorine and has been shown to be effective over a much wider spectrum of micro organisms. Ozone is quite unstable and quickly breaks back down into oxygen. Thus, ozone will not leave a residual after a short time of use nor will increase the salinity of the waters. The decomposition of ozone may suffer several reactions in which free radicals area produced. So in the context of cleaning it may lead to an oxidation of organic matter in cleaning waters thus reducing COD and $BOD_5$ in wastewaters. In order to generate commercial levels of ozone, the corona discharge method is usually used. In addition to the ozone generator further auxiliary equipment is needed: a gas feed preparation system (dry air or oxygen); an injector, a contact tank, off gas destructor and control and measurement equipment. In the design of an ozone based cleaning and disinfection system, it will have to be analyzed the quantity of ozone necessary to guarantee disinfection of the surfaces to be cleaned and the way to apply it, hence the equipment needed to generate and inject the ozone and its costs along with particular hazards prevention measures. Figure 1 shows at a glance the main issues involved in a cleaning in place system including ozonation. The control of CIP systems can vary from simple manual operation to fully integrated PLC. The control of in-place cleaning is a two part operation. The first involves managing the process itself to ensure that every part of the cleaning cycle is performed optimally, it consists of monitoring such things as time, temperature, detergent concentration, flow rates etc. The second part involves assessing whether the procedures have been effective and this is where microbiological controls are often used. Since the purpose of testing samples from CIP systems is to confirm that cleaning has been satisfactory, it is usually sufficient to assay for total contaminants; the presence of any micro-organisms, indicates a failure of the cleaning system.

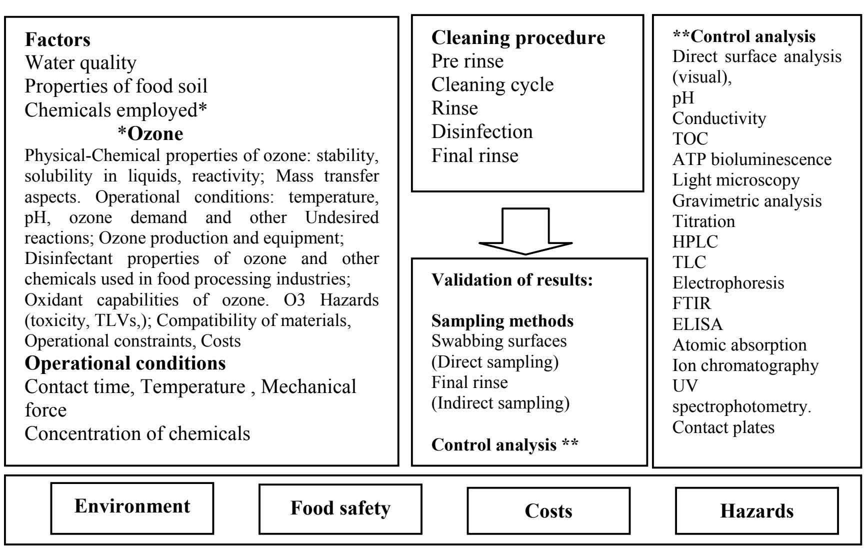


Figure 1: Factors in ozone CIP.

### 3.3 Design and construction of the ozone cleaning in place pilot plant

The design and construction of a flexible pilot plant has been one of the key tasks of the project. The plant allows for the simulation of any kind of cleaning and disinfection protocol employed within food processing industries. Such protocols will be different, as far as the number of steps, products employed and duration of cleaning cycles is concerned, depending on the kind of food product to be. Further to a complete capability of performing any conventional cleaning cycle, the prototype is able to perform cycles that involve the use of ozonated water instead of any of the "conventional" cleaning step. The supply of such element is also controlled by the prototype PLC. Thus, there are three linked subsystem working at the same time: (1)Conventional CIP simulation sub-system; (2) Ozonation sub-system (3) Target sub-system.

Figure 2: Ozone CIP pilot plant.

Table 9: Alternative CIPs.

| **Generic conventional protocol** | **Ozone based protocol** |
|---|---|
| Cold water rinse | ozonated water rinse (recovered) |
| alkaline wash | alkaline wash:100% dose; 75% dose; 50% dose |
| Rinse | ozonated water rinse / no rinse |
| acid wash | acid wash |
| Rinse | ozonated water rinse |
| disinfection wash | ozonated water in closed loop and recovery for initial wash |
| Rinse | no rinse |

Table 10: Expected improvements.

| | |
|---|---|
| Water consumption reduction [1] | 25% |
| Chemical consumption reduction [2] | 25% |
| Volume of wastewaters reduction [3] | 25% |
| Organic load reduction in wastewaters [4] | 5% |
| Salinity of watewaters reduction [5] | 25% |
| Toxicity of wastewaters [6] | Expected |

[1] Considering elimination of conventional final rinse and recovery of ozonated water disinfection; [2] Expected reduction on alkalis plus conventional sanitizers; [3] As for water consumption; [4] In terms of COD reduction. Low reductions are foreseen; [5] Mainly due to reduction in alkali doses; [6] Expected as a consequence of elimination of other sanitizers.

### 3.4 Ongoing work and expected results

Current work focuses on obtaining comparative indicators of the environmental performance of conventional cleaning and disinfection protocols in front of ozone based protocols. The basics of such are described in table 9. Operational conditions such as timing, temperature of solutions and chemical concentration will depend on actual the product under study according to industrial partners' instructions. The expected environmental improvements with similar disinfection and cleanliness efficiency are shown in table 10.

## 4 Conclusions and discussion

Environmental data particular sanitation steps has been collected and confirms that the impact of such operations is significant as the BREF considered qualitatively. Current practices in each particular company play an important role on the level of pollution discharged. The following conclusions may be considered:

- Around 80% of the water consumed in the target sectors is used for cleaning purposes (higher values for wineries).
- Manual operation of CIP is common practice. Great savings in water consumption might be achieved with automation. Installation of measuring devices and keeping registers of consumption values would lead to optimise the use of water and chemicals.
- Last rinse and disinfection solutions are often discharged..
- Values for different cleaning operations have been obtained. Such data only gives a reference idea of the strength of such wastewaters as manually operated CIPs will make the results variable. Peaks in pH (pH =12 and pH = 3) and in conductivity are typical along with high organic load.
- Segregation of first rinse waters polluted with product remnants is key to drastically reduce the strength of wastewaters. Care must be taken with disinfection steps as toxic wastewater may be discharged. Overdosing cleaning and/or disinfecting products is a waste of valuable chemicals and makes it necessary higher quantity of final rinse water to completely eliminate foam and chemical remnants.
- There is not a pattern for the applied amount of water per unit of tank volume, nor for the time the cleaning solutions are kept circulating.

The revisions made on CIP techniques and ozone technologies show that an integration of the technologies would be easy and feasible, adopting safety measures to prevent any hazards arisen by the use of ozone and considering material compatibility of installations with ozone, what is not a serious problem as the considered facilities are made of stainless steel 316. The expected results of ongoing work seeks to obtain indicators that show the differences between conventional and ozone based CIP operations in terms of water and energy consumption, pollution of wastewaters and evaluation of cleaning and disinfection efficiency. So finally, the potential reduction of the environmental impact of sanitation is demonstrated. The expected benefits are: reduction in water consumption. (No final rinse needed.), improvement of the cleaning wastewater quality in terms of COD (mg/l) and Chlorides (mg/l) and Prevention of unhealthy chlorine derivatives (THMs, chloramines…) in cleaning wastewaters, energy savings compared to hot solution consuming operations. The statements in the BREF about CIPs are shown in table 11 in which it is discussed why the "Ozone CIP" technique could be considered more advanced.

Table 11: CIP and Ozone CIP.

| BREF | Comparative Ozone CIP potential advantages |
|---|---|
| 5.1.3.9 "select and use cleaning and disinfection agents which cause minimum harm to the environment and provide effective hygiene control" (1)<br>5.1.3.10 "operate a cleaning-in-place (CIP) of closed equipment and ensure that it is used in an optimal way" (2)<br>5.1.3.14. "avoid the use of halogenated oxidising biocides, except when the alternatives are not effective" (3) | ozone does not leave any residue as it breaks down into oxygen and allows significant water saving as no final rinse is needed and allows to re-use disinfected rinse water for initial cleaning<br>improves final wastewater quality (lower chloride content, it does not generate unhealthy organic-halogen compounds)<br>reduce the risk of accidental discharges in the preparation of disinfection solutions as it is generated on site as needed, eliminating the need for chemical storage |

(1) There are not a explicit mention in section 4.3.8.1 refereed in this BAT to ozone. However, there is a reference to section 4.5.4.8.1 where ozone is considered as an oxidising biocide that "dissipates rapidly after generation, so no chemical residual persist in the treated waste water but its dissolved oxygen content is high. No halogenated compounds are produced. Ozone is also used as an oxidising agent"; (2) So CIP technique is considered as a BAT; (3) This BAT again refers sections 4.3.8.1 and 4.5.4.8.1 previously described.

## Project Consortium and Acknowledgements

The authors would like to thank the Ainia - Instituto Tecnologico Agroalimentario (OZONECIP Project coordinator), Umweltinstitut des Technologie-Transfer-Zentrums Bremerhaven, Gdansk University of Technology, Domecq bodegas, InBev and Meierei - Genossenschaft e.G. Langernhorn. The OZONECIP project is co-funded by the European Union's Life Environment Programme, EC contribution 394,924.00 € (LIFE 05 ENV/E/000251). www.ozonecip.net.

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