OzoneCip: Ozone Cleaning in Place in Food Industries

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Abstract

Cleaning and disinfection operations are of great importance within the food processing industries for food safety reasons but they produce a significant environmental impact in terms of water consumption and wastewater production. Most care areas in food industries rely on a range of chemicals such as chlorine, quaternary ammonium compounds, bromine or iodine products, among others, however, health and environmental concerns are supporting the need for alternative sanitation technologies. Ozone might play an advantageous role in Cleaning in Place operations as an alternative to other sanitizers with several potential environmental advantages. This paper describes the progress made in a Life funded demonstration project with the objective to obtain data that demonstrates the environmental advantages of replacing some conventional sanitizers by ozone concerning cleaning in place systems. An analysis of the different factors involved in an ozone based CIP system is commented, comments in relation to Best Available Technology concerning to cleaning and disinfection are presented, environmental data related to current cleaning operations obtained in collaborating industries of the winery and dairy sectors is shown and a pilot plant designed to perform the demonstration trials is described, finally the potential environmental advantages and the necessary performance indicators are discussed.

Key-words: Ozone, sanitation, cleaning and disinfection, Clean in place, CIP, Food Industry, Wastewater

Introduction

One of the biggest issues currently facing the food industry is that most high care areas continue to rely on a range of chemicals, including various forms of chlorine, branded forms of quaternary ammonium compounds and even bromine or iodine based products, to maintain an acceptable hygiene regime. The sanitising power of these chemicals is not in dispute but side effects are. When chlorine based compounds combine with organic residues the results could potentially be extremely harmful to people. Indeed, research has shown that in certain extreme cases some of these chemicals can develop into carcinogenic and teratogenic compounds that could prove extremely harmful to unborn children for example **[1].** Thus, health and environmental concerns with chemical use on food products are supporting the need for alternative sanitation technologies

In this sense, unlike chlorine, ozone does not react with organic materials to produce undesirable compounds, moreover, unlike other disinfectants, leaves no chemical residual and degrades to molecular oxygen upon reaction or natural degradation. This, coupled with the anti-microbial properties of ozone and growing concerns with chemical use on products and residues in wastewater, is supporting the use of ozone as a sanitizing agent within the food industry for disinfection of surface of products through direct food contact with ozone in aqueous or gaseous form and disinfection of equipment.

In this field, the United States Administration took an important step in favour of ozone that has marked a key turning point in the acceptance of its use by American food manufacturers: in June 2001 the FDA (Food and Drug Administration) formally approved the use of ozone “in gaseous and aqueous phases as an antimicrobial agent for the treatment, storage and processing of foods”. Additionally, in December of the same year the United States Department of Agriculture’s Food Safety and Inspection Service (USDA/FSIS) also approved the use of ozone in contact with meat and poultry, from the raw material to the finished product just before packaging. Previously, the FDA had only approved the use of ozone for disinfecting bottled water and sterilising water bottling lines. In Europe this is the best known and most widely employed food industry application for ozone. It is governed by Directive 2003/40/CE, which sets out the conditions in which ozone-enriched air may be used to treat spring waters and natural mineral waters. This suggests that ozone applications in the food safety field are moving faster in the United States than in Europe, as they have already been expressly recognised by the competent US authorities.

The most researched and commercially 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 in Europe and the United States have demonstrated its efficiency in all types of products (fruits, vegetables, meat and poultry, fish, flour, spices, eggs, cereals, etc.) and in a wide range of operations (raw materials, cleaning and disinfection, product cooling water treatment and food conservation and storage, among others) **[2]**. Direct food contact may be carried out in gaseous or aqueous form, different applications have been reported at experimental and industrial scale with the objective of improving at least one of the following factors: food safety, prevention of cross contamination, extension of shelf life of produce and produce surface sanitation. **[3-10].** Ozone-enriched water systems are provided for fruits & vegetables, meat, poultry and fish cleaning and processing. The systems can be easily integrated into flume, cascade, or drench type operations. Ozone systems can be integrated into both ozone prewash and ozone wash sections. Fogging systems are another method of applying a disinfectant to a surface. Fogging consists of generating and dispersing an aerosol of the disinfectant solution to be applied.

As far as sanitation of food contact and non food contact surfaces in the food industry, after proper cleaning, many different types of sanitizing agents are used, such as, derivatives of chlorine, acid, iodine and quaternary ammonium compounds. Food researchers are searching for alternative cleaning and sanitizing agents effective against food spoilage and pathogenic bacteria, yet harmless to humans and the environment. Ozone is a potential alternative to chlorine for use in the food industry **[21]**. Studies on the ozone gas efficiency in disinfecting stainless steel surfaces have been reported **[12-14]**. Ozone-enriched water can be sprayed directly on floors, drains, walls, wettable equipment, tanks (externally or internally) and clean rooms via a mobile or centralized system with handheld, drop-down or low pressure sprayers **[20]**. Greene **[22]** compared the effectiveness as disinfectants of ozonated water and a chlorinated sanitizer. Stainless steel plates were incubated in UHT-pasteurised milk inoculated with pure cultures of either Pseudomonas fluorescens or Alcaligenes faecalis. The method was designed to simulate the formation of a biofilm containing these bacteria. The active component of the chlorine-based commercial product employed in the experiments was sodium dichloro-s-triazinetrione. The product was applied for a 2 min contact time as specifically recommended by the manufacturer for dairy industry surfaces. The water employed contained 0.5 ppm ozone and was applied for 10 min in each treatment. As the following table shows, the treatments were equally effective in inhibiting both microorganisms, with both treatments destroying over 99% of those present.

Disinfectant	Pseudomonas fluorescens Reduction (Log cfu/cm2)	Alcaligenes Faecalis Reduction (Log cfu/cm2)
Chlorine-based product (2 min)	4.6	4.2
Ozonated water (10 min)	5.6	4.4

Table 1.Compared effectiveness of ozonated water and a chlorinated sanitizer (Green, 1993)

The authors conclude that ozonation is an effective sanitisation method that may have potential use in the dairy industry and that its advantages include an absence of undesirable by-products such as the trihalomethanes formed by chlorine-based products. They also note that ozone treatment can bring cost-savings as maintenance costs are low.

In another laboratory-scale model, Takahashi et al., **[23]**, compared the efficacies of gaseous ozone and sodium hypochlorite as oxidants in cleaning stainless steel particles impregnated with different proteins. Exposure of the particles to 0.5% (v/v) ozone gas for 30 min improved the removal of proteins during subsequent cleaning with a NaOH solution to a degree equivalent to that achieved by a sodium solution containing 0.2 to 0.4 g/l sodium hypochlorite. Moreover, they observed that the effect of the ozone pre-treatment on protein removal depended on the ozone concentration. When pre-treatment was carried out with a high ozone concentration (20%) for 30 min, the proteins were almost completely eliminated from the stainless steel particles. These results show that the complementary action of the alkalinity and the oxidants provided adequate, effective cleansing of protein fouling. They also indicate that gaseous ozone could potentially be used as an alternative to sodium hypochlorite for removing protein soiling from stainless steel surfaces.

For **CIP** applications, ozone enriched water is directly injected into a facility's fluid distribution network and circulated for a set duration time. Overall chemical costs and sewage disposal costs are reduced also overall system deterioration is reduced when using ozone-enriched water rather than hot water or traditional anti-microbial chemicals **[15]**.

The advantages of using ozone in CIP systems, compared to traditional disinfectants, are that it leaves no residues and is applied in cold water. When chemical products (chlorine or iodophore solutions) are used instead of ozone, multiple rinses are required to remove product residues. This consumes greater quantities of water and always entails the risks associated with a lack of effectiveness. Equally, using high-temperature water or steam is very expensive, as considerable energy consumption is required to produce them and the expansion and contraction of welds can cause deterioration of the lines.

Different studies reported show that cleaning in place using ozone as disinfecting agent might be an interesting choice to improve the environmental performance of cleaning operations carried out in food processing industries. Thus, Richard Packman and Dave Adams **[16]** outline the benefits of the use of ozone in order to reduce the amount f water needed for cleaning of vessels compared with a conventional system. Lagrange, et al., **[17]**, researched the use of ozonated water as a disinfectant in the context of CIP systems. The tests conducted on Staphylococcus aureus, Pseudomonas aeruginosa and Candida albicans showed that while ozonated water possesses high antimicrobial properties, these can be inactivated by the presence of proteins. Consequently, the authors recommend efficient cleaning before using ozonated water for disinfection purposes. Under the conditions defined in their experiments, the use of ozonated water was capable of lowering microbe counts by 99%. Shaun Porter **[18]** reports the effectiveness of the use of ultraviolet followed by ozonation of rinsing water to be used in a brewery; the ozonated water is used for bottle rinsing and at various CIP locations throughout the plant such as final rinsing of stainless steel fermentation tanks. Also, the use of ozone is reported in wineries for barrel washing, winery washdown, bottle rinsing and CIP systems. John McClain **[19]** reports the use of ozone for sanitation operations in wineries (process and equipment sanitation), the advantages of using ozone are documented and discussed, along with safety considerations.

In Australia, ozone is being used successfully on an industrial scale as an alternative to chlorine for disinfecting the oak barrels used for ageing the wine. The main advantage that is that it is more effective for controlling certain Brettanomyces yeast species that cause off-tastes and other defects in wines. **[24]**. A further, no less important advantage is that changing to ozone disinfection avoids the presence of substances such as Trichloroanisol (TCA), which is responsible for cork taint problems in many wines. Ozone is also considered to provide cost-savings as it reduces the need to buy and store chlorine.

Most studies focus their attention on the capabilities of ozone as a disinfecting agent and almost no data has been obtained on the environmental implications of the cleaning and disinfection operations. Nevertheless, sanitation in food industries has significant environmental considerations as frequent cleaning is required and this employs water intensively along with chemicals **[25]**.

The most important cleaning tasks are related to the washing of process vessels, tanks and the net of pipes that are involved in the production process. In such closed equipment **C**leaning **I**n **P**lace **(CIP)** systems are of common use. **CIP** are characterized by automatic cleaning programs based on a succession of several solutions of water, cleaning chemicals and disinfection agents. These chemicals are discharged into sewer systems together with large amounts of water necessary to rinse out residual chemicals from the machines. Typically, cleaning and disinfection wastewaters contain soluble organic material, FOG, SS, nitrate, nitrite, ammonia and phosphate from product remnants and removed deposit soil, as also contains residues of cleaning agents, e.g. acid or alkali solutions the wastewater may have a high or low pH and high conductivity. The use of phosphoric and nitric acids will increase the phosphate and nitrate content of the wastewater.

Adopting ozone in cleaning and disinfection processes can bring various advantages over commonly employed disinfectants: ozone breaks down quickly into oxygen without leaving undesirable residues, this is an advantage both from the point of view of food safety and to improve the quality of wastewaters by avoiding the presence of harmful chlorine compounds; replacing chemical products with ozone also lowers the concentration of salts and, therefore, the electrical conductivity of discharges; the use of ozone can save water in comparison to other biocides, as it does not leave residues it does not require a final rinse to remove any residual disinfectant that might remain, also, ozonated water, which has been used for disinfection, can potentially be re-used for the initial cleaning stages. Ozone use could also provide energy savings as it is normally used at low temperatures.

The reduced environmental impact is a significant factor that may favour the future development of ozone in all countries, especially in Europe. European environmental legislation is increasingly requiring polluting industries to move to clean technologies. The most important regulation in this respect is the IPPC Directive, which has considerable relevance and far-reaching effects for the major European food manufacturers. Directive 96/61/EC concerning Integrated Pollution Prevention and Control (IPPC) could indirectly encourage ozone use in EU countries, if it was considered a Best Available Technique (BAT) for food industry disinfection operations. As its name indicates, the IPPC directive attempts to encourage technologies that reduce pollution, preferably those that do so at source. For this reason, it refers to BATs as a criterion when granting companies operating licences. BATs are defined as economically viable, commercially available techniques that enable competitive levels of quality and productivity to be achieved and are noted for their greater environmental efficacy. Although industrial installations affected by the IPPC directive are not obliged to adopt BATs in order to obtain a licence, they are required to achieve environmental results similar to those of BATs. BAT techniques will therefore have a further point in their favour when business investment decisions are made, making them more competitive.

Ozonecip is a demonstration project funded by the EC under the LIFE-Environment Programme. Its objective is the reduction of the environmental impact of cleaning operations through an innovative technique consisting on the use of ozone as an alternative sanitising agent instead of traditional chemicals. Among the food industries cleaning procedures, Cleaning In Place (CIP) is considered as BAT in the European reference documents and “Ozonecip” technique is expected to be more advanced than the BATs described. This project aims to bridge the gap between research and development results and widespread implementation/market introduction, identifying the obstacles leading to solutions to overcome those barriers.

Material and methods

Demonstration activities will focus on three key sub-sectors: dairy products, brewery and winery. The planned tasks are:

A. Preliminary actions. In order to get the necessary multidisciplinary background different specific studies and reviews are produced: BAT documents, ozone technologies, CIP techniques, environmental diagnosis of cleaning operations in collaborating food industries
B. Ozonecip prototype. A prototype will be created at AINIA’s facilities to simulate conventional CIP processes and essay alternative processes based in ozone
C. Demonstration activities. Simulation of protocols comparing the environmental results obtained when performed with and without ozone.
D. Evaluation. Water and chemicals consumption, hygienic results, wastewaters
E. Dissemination www.ozonecip.net

The tasks finished so far are task A and B: One of the key issues of the project is the pilot plant where the demonstration trials will be performed. Experimental results are necessary so that ozone CIP environmental benefits can be demonstrated. A number of variables will be controlled, measured or analysed. Collected data will allow the definition of environmental indicators and representative values and reach conclusions about the environmental benefits. The prototype allows simulating industrial CIP processes carried out at food plants and assay processes based on ozone. The prototype system consists of three subsystems: CIP pilot system, ozone generation and injection system and the target equipment to be cleaned (Figure 2). Non-environmental factors that can affect the applicability of the ozone CIP alternative will be considered.

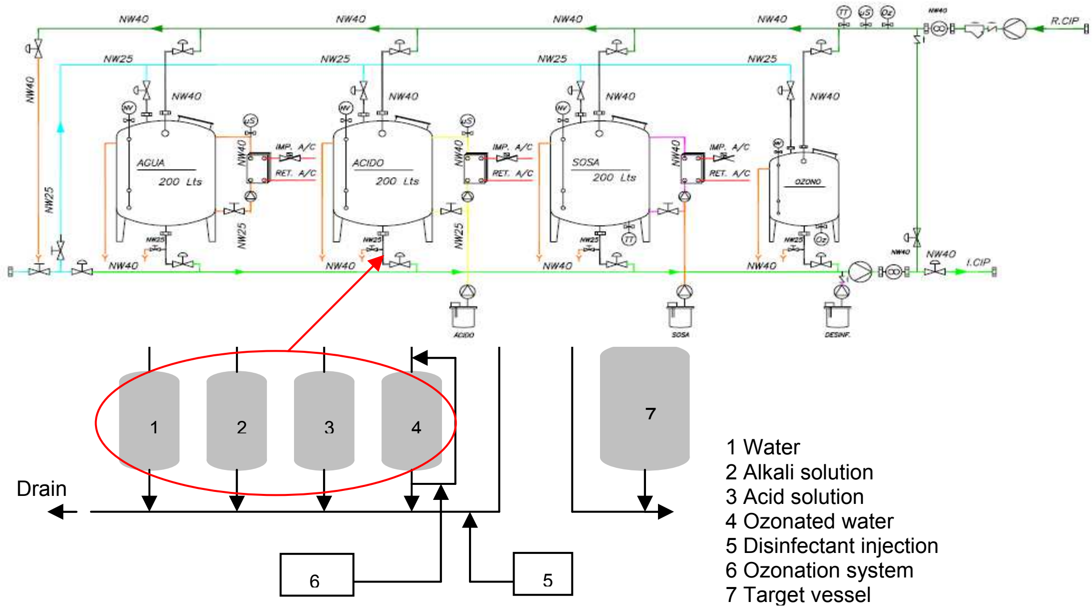

Figure 2. Pilot plant. Main subsystems, and CIP flow sheet

The operations provided by the CIP prototype will be: pre-rinse, alkaline cleaning, intermediate rinse, acid cleaning, rinse, hot water sterilisation/chemical sterilisation, final rinse. Solutions and rinse water may be warmed and it will be able to perform cycles that involve ozonated water instead of any of the "conventional" cleaning steps Although the system may be connected to any kind of target to be cleaned, a typical stainless steel holding tank provided with a cleaning spray ball will be considered as this is a kind of closed equipment broadly employed in all food and beverages sectors.

Results and discussion

Cleaning and disinfection and best available techniques in food industries

Current documents on best available techniques have been consulted in order to get a clear picture of actual practice in cleaning and disinfection within the sectors under study (wine, beer and dairy products) and what is already recognized as BAT in this field. Some ideas may be outlined here in connection to this issue:

- It is stated that along with environmental considerations all FDM production installations must comply with the required food safety standards. These may have an influence on environmental considerations, e.g. frequent cleaning is required and this uses heated water and detergents. This means that cleaning and disinfection is a must within food industries and that will cause an environmental impact, at least in terms of water consumption, waste water generation and, depending on the industry, energy consumption
- The key environmental issues in the FDM industry included in the Reference Document on Best Available Techniques in the Food, Drink and Milk Industry (FDM-BREF) are*: "water consumption and waste water production, air pollution related to VOCs and odour, noise, solid output, and energy consumption".*
- As far as water consumption is concerned FDM-BREF already says that: "*most of the water which is not used as an ingredient ultimately appears in the waste water stream*". (This is the case for cleaning and disinfection waters).
- In relation to the use of water for cleaning and disinfection the FDM-BREF states that:*"large quantities of water are required for cleaning and disinfection. In many installations this is the main consumer of water, with the amount depending on the type and size of equipment to be cleaned and the materials processed. Cleaning and disinfection produces waste water. In principle, the cleaning and disinfection agents that are used are discharged via the waste water, either in their original state or as reaction products. Also, when cleaning is carried out at elevated temperatures there will be a high consumption of energy to heat water and produce steam".*
- Regarding to cleaning and disinfection. In all FDM installations, BAT is to do the following:
    - Fit cleaning hoses used for manual cleaning with hand operated triggers
    - Supply pressure-controlled water and do this via nozzles

- Select and use cleaning and disinfection agents which cause minimum harm to the environment and provide effective hygiene control
- Operate a cleaning-in-place (CIP) of closed equipment and ensure that it is used in an optimal way by, e.g. measuring turbidity, conductivity or pH and automatically dosing chemicals at the correct concentrations.
- Use single-use systems for small or rarely used plants or where the cleaning solution becomes highly polluted, such as UHT plants, membrane separation plants, and the preliminary cleaning of evaporators and spray driers
- Where there area suitable variations in the pHs of the waste water streams from CIP and other sources, apply self neutralisation of alkaline and acidic waste water streams in a neutralisation tank
- Minimise the use of EDTA, by only using it where it is required, with the frequency required and by minimising the quantity used, e.e. by recycling cleaning solutions
- Avoid the use of halogenated biocides, except where the alternatives are not effective.

The statements in the BREF in relation to Best Available Techniques (BAT) about cleaning and disinfection, and in particular about Clean In Place (CIP) systems, are resumed in the following table in which it is discussed why the "Ozone CIP" technique could be considered more advanced than BAT described in this BREF :

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) 5.1.3.10 "operate a cleaning-in-place (CIP) of closed equipment and ensure that it is used in an optimal way" (2) 5.1.3.14. "avoid the use of halogenated oxidising biocides, except when the alternatives are not effective" (3)	• because as ozone does not leave any residue since it breaks down into oxygen after its disinfection action: • Ozone CIP systems allow significant water saving because not final rinse is needed-Ozone CIP systems improves final wastewater quality (lower chloride content, it does not generate unhealthy organo-halogen compounds)-Ozone CIP could allow to re-used disinfection water flow for the initial cleaning stages, either directly or after re-ozonating it to attain the required quality.·provides energy savings in CIP systems as it is normally used at low temperaturesas ozone is generated on site as needed, eliminating the need for chemical storage and the risk of accidents. • reduce the risk of accidents in the preparation of disinfection solutions.Is generated on site as needed, eliminating the need for chemical storage and the risk of accidents • after ozone conversion back into oxygen, an extra concentration of the last is in the wastewater reducing odours and facilitating the biological treatment at the sewer

(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.

Table 2.Best available technologies and ozone cip

Cleaning in place techniques and ozone technology

State of the art reviews were carried out on current practice of CIP techniques, ozone technologies and its applications. Figure 3 shows at a glance the main issues involved in a cleaning in place system and, in particular, in an ozonecip system. A lot of literature on such topics may be found elsewhere so further comments on this is out of the scope of this paper. From the information collected, in addition to the factors to consider in order to define a CIP system the following issues are found to be important to integrate ozone technology and in a clean in place system:

- Physical-Chemical properties of ozone: stability, solubility in liquids, reactivity; Mass transfer aspects.
- Operational conditions: temperature, pH, ozone demand and other
- Undesired reactions;
- Ozone production and equipment;
- Disinfectant properties of ozone and other chemicals used in food processing industries;
- Oxidant capabilities of ozone.
- Ozone Hazards (toxicity, TLVs,);

- Compatibility of materials,
- Operational constraints,
- Food safety considerations and, regulations.
- Costs,

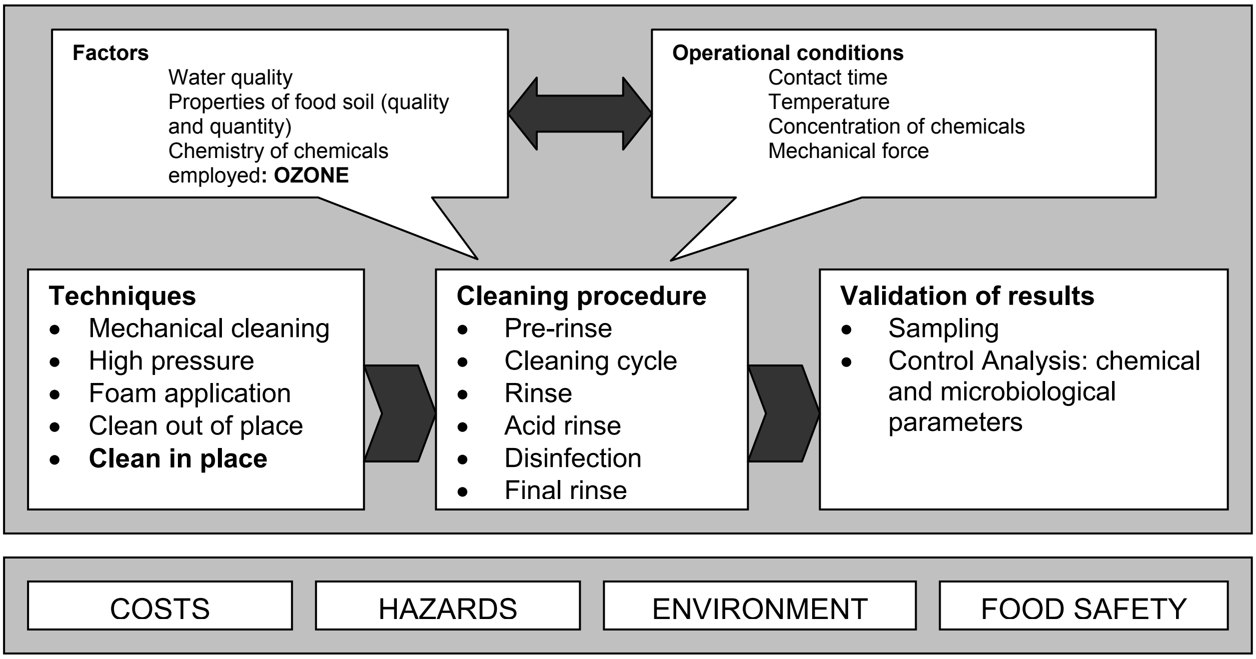

Figure 3. Factors to consider to define a cleaning and disinfection system within food industries

Thus, for each particular type of soil to be cleaned on a particular kind of surface, along with other factors, considering the food safety regulations, an efficiency must be reached through the proper cleaning and disinfection technique with the chemicals of choice, these will influence the operational conditions and will determine the cleaning procedure whose efficiency must be validated and monitored. The cleaning and disinfection system as a whole will have its costs of investment and costs of exploitation, derived hazard must be allowed for and the system will cause a particular environmental impact. If ozone is to be considered, considering its chemical properties, 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 that way the related costs. Particular hazards prevention measures apply.

Environmental impact of conventional cleaning operations

As far as environmental data reported at the FDM-BREF is concerned 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, sampling and analytical methods and statistical presentations. In this sense, different amount of process and environmental information is already available at the FDM-BREF for brewery, winery and dairy sub-sectors; indeed the data related to wineries is inexistent.

Through the visits to facilities and interviews with technicians carried out within the scope of this project to industries of the three sub-sectors we have observed that, in general, 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 degree of automation of the processes, the available resources and the degree of monitoring is higher for breweries, slightly lower for big sized dairies, less for small dairies and, from low to almost inexistent (depending on the size of the winery) in the winery sector where traditional and manual ways of doing things have been found at a higher extent. Furthermore, in the winery sector there is a particularity that differs from the other two sectors under study. That is that wineries may be divided into two general groups: bottlers and elaborators. The latter is formed, mainly, by small wineries that transform grape juice into wine and sell wine to bottlers, this group work mainly, in parallel with the harvesting season and keeps certain activity the rest of the year because of ageing and racking operations. Bottlers keep a similar degree of activity throughout all the year.

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 at getting environmental in-process information at industrial level through field work (visits and sampling) in an order of preference as follows: 1 Winery, 2 Dairy. Brewery data could be obtained in literature. For the development of the industrial diagnosis we have had the collaboration of a number of companies that have accessed to show under their particular methods and protocols for cleaning and disinfection.

Environmental data linked to the cleaning and disinfection of closed equipment in the winery sector

In the BREF, water consumption is presented as one of the key environmental issues for the FDM sector. Here, it is said that specifically, in winery sector, water is used for cooling the stabilisation tanks and for **cleaning operations**. Nevertheless, no reference quantitative data on consumption of water within winery industry in relation to production capacity is given at the BREF document nor data on consumption of water specifically for cleaning purposes. Nevertheless, most of consumption is devoted for cleaning purposes.

In relation to wineries (wine elaborators) where grapes are transformed into wine and no bottling lines are present, bulk wine is sold to bottlers that will finish the stabilisation of the wine and will perform the bottling operation, this wineries consume around 80% of the water during the period between September and November (with the grape harvesting season and first phase of fermentation of young wines), after that racking and ageing will keep some activity in the winery but low compared to the high season. Wine bottlers, do not receive grapes, just wine from elaborators, in this kind of wineries racking, cold stabilisation, ageing and filtration of wines is performed and the final product is bottled. This kind of wineries keep a constant activity all throughout the year and consume higher volumes of water because of the cleaning and disinfection of bottles and bottling lines. Table 3 shows data collected by ainia from different wineries in relation to overall consumption of water at the winery in relation to their respective production capacity.

	m3 water consumed/m3 wine produced
Wine elaborator	0.09-0,37
Wine bottler	0,35-1,23

Table 3.Water consumption in wineries (source, ainia)

If water is not used as an ingredient, ultimately appears in the waste water stream, so large volumes of water consumed in wineries represent large quantities of waste waters. Waste water flow rates may be very variable on a daily, weekly or seasonal basis. The waste water profile is largely dependent on production and cleaning patterns. In winery ellaborators, processing takes place on a campaign basis and there is little waste water generated for part of the year, apart from the cleaning of tanks.

At wineries waste water is generated in nearly all process steps, e.g. cleaning of containers, reactors and filters. Composition of the waste water typically contains soluble organic material, FOG, SS, nitrate, nitrite, ammonia and phosphate from product remnants and removed deposited soil. It also contains residues of cleaning agents, e.g. acid or alkali solutions. The highest concentrated waste water is produced during fermentation, fining and ageing/racking due to the washing out of the sediments (lees). We have analysed samples of wine in order to know the degree of organic load transferred to the cleaning waste waters as a consequence of product remnants in the tanks or pipes (table 2). The semi-solid fractions can be separated rather than being washed with water, due to their high organic load. If solids from fining and racking are not separated, the waste water is highly contaminated and has extremely high BOD values of up to 500.000 mg/l. Therefore, it is essential to recover the waste water components at source.

Wine bottles are cleaned before filling, and consequently washing water enters the drains. Wineries waste water shows an acidic character (pH 4 – 6) except when caustic solutions are used in the elimination of tartrate or during the conditioning of bottles. The most polluting waste water during wine production is generated during the fermentation and racking (especially first racking) operations. Range figures for wineries of the Valencian Region is given in table 4

		Pollution by product remnants			Wastewaters	
		Red wine	**Rose wine**	**White wine**	**Elaborator**	**Bottler**
pH		3,4	3,4	3,6	4.06-8.01	7,21-8,14
Conductivity	mS/cm	2,1	2,3	2,3	429-5090	525-2000
COD	mg/l	171000	176000	183000	76-30750	32-1245
TKN	mg/l	580	520	520	2-53	7-66
P	mg/l	90	100	90	2,2-82	1-3,6
Toxicity	U.T				0-250	0-30

Table 4.Characteristics of product remnants and general wastewaters in wineries (source, ainia)

Quantitative ranges obtained show the dramatic influence of performing good environmental practices and a proper segregation of lees and first wash solutions prior to discharge into drains. Also, difference of results obtained in bottlers and elaborators shows that the environmental impact is rather higher for the elaborators.

Taking into account that wine remnants would have a COD around 175.000 mg O2/l, and that usual limit values for discharge at public sewers for COD is of 1000 mgO2/l, it would mean that each litre of wine remaining at the tank or pipe would pollute up to 175litres of fresh water so that, by dilution, the waste water generated could have its COD values under the discharge limits for COD.

As far as quantitative environmental data of wastewaters produced in particular by the cleaning operations the following data has been obtained by ainia from different visits to wineries and interviews with technicians. Although sampling and analysis of particular streams of discharged wash waters has been performed results will show just an idea of the impact produced by this operations but, as manual operation is common practice in industry the amount of water employed in rinsing is very dependant on the operator actually doing the operation. Different cases have been monitored: manual pressure cleaning and cleaning with spray ball, cleaning with or without recovery of initial rinse (i.e. with lees remnants), cleaning after alkali wash and some more complex protocols including disinfection step.

The following table shows the results for such diverse operations.

		Characteristics of cleaning wastewaters										
		1	**2**	**3**	**4**	**5a**	**5b**	**5c**	**5d**	**6a**	**6b**	**6c**
pH		7,7	4,4	7,2	13	4,6	7,1	5	6,8	6,9	7,6	7,7
Conductivity	mS/cm	853	1470	487	24900	1300	1120	1140	1120	2543	2700	2625
COD	mg/l	135	2610	5187	110	19560	239	1053	10	6275	682	139
TKN	mg/l	5		4,5		24	<2	<2	0	2,6	<1	
P	mg/l	<1		1,5		12,7	<1	4,8	0	1,5	8	>1700
Toxicity	U.T	<2		0				>1700	<2		>1700	215

1 Manual pressure final rinse with water. 10000 L most tank. Pre-rinse segregated for alcohol recovery
2 Manual pressure rinse with water. 50,000 L cold stabilisation tank. red wine. Pre-rinse segregated for alcohol recovery.
3 Manual CIP. Spray ball. Without prerinse recovery
4.Manual CIP. Spray ball. 25,000 L cold stabilisation tank. With prerinse recovery and alkaline wash recovered.
5 Manual CIP. Spray ball. 17.000 L wine storage tank. No recovery
5a Rinse with cold water
5b Rinse with hot water (80ºC)
5c Disinfectant solution wash (peracetic)
5d Final rinse
6 Manual CIP. Spray ball. 600,000 L filtered wine storage tanks. No recovery
6a Rinse with water
6b Disinfectant solution wash (quaternary ammonia)
6c Final rinse

Table 5.Characteristics of cleaning wastewaters in wineries (source, ainia)

Environmental data linked to the Cleaning and disinfection of close equipment in the dairy sector

At the F&D BREF it is already stated that water consumption in dairies is mainly associated with cleaning operations. The following table shows some general ratios on water consumption in dairy industries depending on the type of product manufactured; although a narrower range of ratios of water consumption is reported to be around 1-5 l/kg milk as reasonably efficient,

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

Table 6: Water consumption in European dairies (European Dairy Association, 2002).

As far as the water consumption to cleaning in place operations the amount of water actually consumed is very variable depending on factors such as: manual or automatic operation, recovery of cleaning solutions performed or not, training of operator. Table 7 shows the data on water consumption in two collaborating dairy companies along with the volume of wastewaters.

	Water consumption (m3/year)	Waste water production (m3/year)
Dairy company 1	6,500	5,213
Dairy company 2 (cheese)	16,131	15,858

Table 7: Water consumption and wastewater production in collaborating dairy companies

Company 1assumes that all its waste water is produced as a consequence of cleaning and disinfection operations, that means that 80 % of the water consumed is used for cleaning and disinfection and 100% of the industrial water discharged is produced because of this operation. In this company 2.000.000 l of raw milk is used per year thus a ratio of 3,25 l of water consumed per litre of milk processed is obtained. Company 2 also estimates that all wastewaters are produced as a consequence of cleaning and disinfection operations, in this case, that means that more than 95% of the water consumed is spent for cleaning purposes.
Most of the chemicals used in a dairy industry are used for the cleaning and disinfection of process machinery and pipelines and are finally discharged in solution in the wastewaters. Fresh product dairies mainly use caustic and nitric acid and some disinfectants, such as hydrogen peroxide, peracetic acid and sodium hypochlorite. Next table shows the consumption of cleaning agents used in European dairies. Of the total chemical consumption in Nordic dairies, 55 % is caustic and 30 % nitric acid.

Products	Consumption of cleaning agents (kg/t processed milk)		
	NaOH, 100 %	HNO3, 100 %	Detergents
Market milk and yoghurt	0.2 – 10	0.2 – 5.0	*
Cheese	0.4 – 5.4	0.6 – 3.8	0.1 – 1.5
Milk and whey powder	0.4 – 5.4	0.8 – 2.5	*
Values vary with the length and capacity of production runs *Not applicable			

Table 8: Consumption of cleaning agents used in European dairies [European Dairy Association, 2002]

The F&D BREF already states that waste water is the main environmental issue in the dairy sector. The sector uses a vast amount of water, and generates a huge amount of waste water in maintaining the required level of hygiene and cleanliness. Thus, 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. Wastewater volume in a well managed installation is reported to be about 1 – 2 l/kg pf milk processed. Furthermore it indicates that white products processing (milk, cream and yoghurt) is less polluting than yellow products processing (butter and cheese) and this is less polluting than special products processing (concentrated milk, whey and dried milk) in terms of volume of waste waters produced per kg of milk processed. Some reference values are given below:

Type of product	Waste water volume (l/kg of milk processed)
white products (milk, cream and yoghurt)	3
yellow products (butter and cheese)	4
special processing (concentrated milk, whey and dried milk)	5

Table 9: Approximate volumes of waste water in dairy activities (FDM-BREF)

The pollution load on the waste water is high due to residual milk fat and proteins as well as cleaning chemicals. The organic load caused by the cleaning chemicals is minor; the main problem is the fluctuation of the pH of the waste water, which disturbs the balance of the waste water treatment plant. Tables 10 and 11 show the load transferred by dairy products to water:

Product	BOD5 (mg/kg of product)
Whole milk	104,000
Skimmed milk	67,000
Double cream	399,000
Yoghurt	91,000
Ice-cream	292,000
Whey	34,000

Table 10: Typical BOD levels of various milk products (13, Environment Agency of England and Wales, 2000)

	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 11: Typical levels of various milk products (ainia)

The storage of concentrated chemicals also represents a risk, both for the environment and the occupational safety. The cleaning solutions can be replaced by commercially available CIP-detergent mixtures, in which the cleaning properties of alkaline and acid detergents are combined. However, some of these mixtures contain phosphates and tensides, which increase the load on the waste water.

In the table bellow reference values for volume and pollution levels of dairy wastewater in Europe are shown:

Product	Waste water volume (l/kg)	Parameters (mg/kg of processed milk)		
		COD	Total N	Total P
Market milk and yoghurt	0.9-25	2.0-10	0.05-0,14	0.01-0.02
Cheese	0.7-60	0.8-13	0.08-0.2	0.01-0.05
Milk and whey powder	0.4-60	0.5-6	0.03-0.3	0.01-0.2
Ice-cream	2.7-7.8			

Table 12: Volume and pollution levels of dairy wastewater in Europe (Nordic Council of Ministers, et al., 2001, 160, European Dairy Association, 2002)

Typical characteristics of untreated waste waters from dairy industries are shown below:

Component	Range
SS	24-5700 mg/l

TSS	135-8500 mg/l
COD	500-4500 mg/l **
BOD_5	450-4790 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 (up to 2000*) mg/l
pH	5.3- 9.4 (6-10*)
Temperature	12 - 40 ºC
Actual levels will depend on the use of in-process techniques to prevent water contamination (not reported) * CIAA comments (83, CIAA, 2001) ** German comments (99, Germany, 2002)	

Table 13: Reported untreated dairy wastewater contamination levels. Environment Agency of England and Wales, 2000)

In connection to this it has been obtained the following data in 2 dairy companies. Company 1 produces milk in bags and yogurt. The characteristics of the final wastewaters show high variability as it is very dependant on the particular operation being carried out with high peaks. Company 2 produces cheese.

	Company 1. Sample A	Company 1. Sample B	Company 2
SS (mg/L)	2,074	22	332
BOD_5 mg O_2/L	17,072	560	1,180
COD mg O_2/L	2,780	594	2,772
Conductivity (µS/cm)	6,030	715	71.8
Phosphorous (mg P/L)	130	3,4	14.06
NKT (mg/L)	484	12	1,656
pH	6.95	7.64	5.34
Toxicity	2.6	<2	10.5

Table 14: Wastewater contamination levels in dairy companies

Regarding to cleaning operations the following data was obtained in a yogurt and milk producer:

	1 Rinse with hot water	2 alkaline wash	3 Rinse with hot water	4 Wash with acid solution	5 Rinse with hot water	Composite
pH	8.12	12.81	10.83	2.46	497	12.12
Conductivity µS/cm	546	39,200	1,318	4,840	6.94	5,640
COD mg O_2/L		568	36	428	31	
Pt mg P/L		7	<2	1,206	55	
NKT mg N/L		23	3	<2	<2	
Toxicity		>2,000		>2,000		>2,000
Spent volume L	100	100	100	100	100	500

Table15. Wastewaters of the cleaning of a 1,000 L milk fermentation tank for yogurt production

	1 Pre-rinse	2 Alkaline wash	3 Final rinse
pH	8.57	13.11	8.63
Conductivity (µS/cm)	456	13,280	485
COD (mg O_2/L)	76	196	32
Volume spent water (Litres)	500	500	500

Table16. Characteristics of the wastewaters of cleaning of a transport container of raw milk)

	1 Pre-rinse	2 Acid wash	3 Rinse	4 Final rinse
pH	8.19	2.49	3.29	7.99
Conductivity (µS/cm)	430	9,920	1,170	412
COD (mg O_2/L)	876	958	154	44
Volume spent water (Litres)	500	500	500	500

Table17.Characteristics of the wastewaters of cleaning a milk storage tank

Table 18 shows the strength of the cleaning waters discharged for different process equipment in cheese processing company. The volume of rinsing waste waters per step is not measured but it is considered to be around 500L each time, cleaning solution are reused, one CIP system is employed for everything except for the pasteurizer that is cleaned independently.

	pH (ud)	Conductivity (µS/cm)	COD (mg O_2/L)
(Truck) raw milk tank			
1 Pre rinse	11.61	1,700	1,465
2 Rinse after Alkaline wash	12.45	5,200	1,176
3 Final rinse	8.57	1,016	30
Storage milk tank			
Pre-rinse	8.18	1,095	1,416
Rinse after alkaline wash	12.45	5,120	1,124
Rinse after acid wash	2.83	3,770	282
Final rinse	8.07	1,040	44
Coagulation of milk tank			
Pre rinse (CIP)	9.42	1,005	340
Rinse after alkaline wash	12.03	1,872	218
Rinse after acid wash	3.60	1,269	168
Final rinse (after disinfection)	n.a	n.a	n.a
Pasteurizer			
Pre rinse (CIP)	8.24	882	28
Rinse after alkaline wash	13.22	18,760	1,190
Rinse after acid wash	2.65	5,470	428
Final rinse (after disinfection)	7.59	949	60
Disinfecting solution	6.73	945	338

n.a = not available

Table 18. Wastewaters at different steps in different cleaning operations in a cheese processing factory

Environmental data linked to the Cleaning and disinfection of close equipment in the brewery sector

In the BREF it is stated that breweries use significant amounts of water and that water consumption for modern breweries generally ranges from 4 to 10 l/l of beer produced. This interval shows that, there are, in fact many factors that may affect the water necessities in breweries. This range encompasses small and large breweries that have different cleaning and disinfection procedures, which are the main water demanding activities. However, breweries using CIP cleaning systems are able to reduce significantly their water consumption values. Optimised and tailor-made CIP programs are strongly required in order to get substantial reduction in water consumption. Data reported by some breweries are consistent with this reference values. The Inbev Germany (Beck's & Co.) brewery located in Bremen (Germany) reports that the reduction in the water consumption is, mainly, due to their CIP process' improvement that enables the reduction of the water demand, by optimising the CIP programs used for cleaning and disinfection operations.

Specific water consumption in brewery 1 (hl water/hl beer)			
2001	2002	2003	2004
5,47	4,77	4,46	4,47

Table 19. Specific consumption of water reported by Grupo San Miguel (Source: Informe medioambiental 2004. Grupo Mahou San Miguel)

Specific water consumption in a brewery 2 (hl water/hl beer)			
2003	2004	2005	2006
4.11	3.95	3.95	3.91

Table 20. Specific consumption of water reported by Inbev (source: ozonecip internal reports).

Specific water consumption in brewery 3 (hl water/hl beer + soft drinks)			
2003	2004	2005	2006
5.41	5.47	5.49	5.00*

***target value**

Table 21. Specific consumption of water reported by Heineken Group (Heineken Sustainability Report 2004-2005).

Water consumption levels for individual process stages have been already identified. Reference values in German brewing industry are shown in table 22:

Department	**Specific water consumption (m^3/hl beer produced)**			
	Measured**		**Literature**	
	From	*To*	*From*	*To*
Brewhouse	0,130	0,236	0,174	0,26
Cold storage			0,11	0,24
Fermentation cellar	0,032	0,053	0,04	0,08
Storage cellar	0,024	0,067	0,01	0,06
Filtering cellar	0,031	0,109	0,01	0,076
Bottling cellar	0,059	0,163	0,09	0,098
Cask cellar	0,013	0,061	0,01	0,12
Miscellaneous*	0,20	0,204	0,026	0,397
Total Process	**0,489**	**0,893**	**0,470**	**1,331**

* Estimates
** Measurements by Heidemann, Rosenwinkel and Seyfried (1990 to 1992)

Table 22. Specific water consumption in German brewing industry (1990-1992)

The wastewater discharge is equal to the water supply minus the produced beer, the evaporated water and the water present in the by-products and solid waste. It is reported in the BREF-document that in an Austrian brewery about 0.26- 0.6m^3 of wastewater is produced per hectolitre of beer sold. It is also reported that in modern breweries 0.3-0.9m^3 of wastewater is produced per Hl of beer. According to the Spanish reference book for the brewery sector (Guía de MTDs del sector cervecero) the total volume of waste water generated in Spanish breweries rang from 2.5 to 7.2 Hl of waste water/Hl of beer produced. The wastewater emission values for the Inbev Germany Brewery (Beck's & Co.) and for Mahou San Miguel Group are shown below:

Year	Wastewater emission [hl wastewater/ hl beer produced]
2003	2,71
2004	2,64
2005	2,81
2006 (Jan.- Apr.)	2,72

Table 23. Waste water emission values for Inbev Germany (Beck's & Co.)

Year	Wastewater emission [hl wastewater/ hl beer produced]
2001	3,93
2002	3,28
2003	2,92
2004	2,99

Table 24. Waste water emission values for Mahou-San Miguel Group (Informe Medioambiental 2004)

In the FDM BREF document it is stated that the wastewater is very variable in its composition and the pollutant's load of the different steps do not follow the volumes throughput, e.g. bottle cleaning produces a high amount of wastewater but with only a low organic load, while wastewater from fermentation and filtering account for only about 3 % of the total wastewater volume but 97% of the BOD load. Suspended solids in wastewaters may origin from discharge of by-products (e.g. diatomaceous earth and label pulp from bottle cleaning). Nitrogen originates mainly from detergents used for tank cleaning, from the malt and from additives. Phosphorus may come from the cleaning agent used. Large variations in pH may occur due to the use of acids and caustic for the cleaning of process equipment and returnable bottles. Heavy metals are normally present in very low concentrations. Wear of the machines, especially conveyors in packaging lines, may be source of nickel and chromium. Table 25 shows the concentration reference range of pollution load in wastewaters in a brewery:

Parameter	Unit	Range
BOD_5	mg/ l	1000-1500
COD	mg/ l	1800-3000
Suspended Solids	mg/ l	10-60
Total Nitrogen	mg/ l	30-100
Total phosphorous	mg/ l	30-100
pH	-	3-13

Table25. Untreated wastewater characteristics for breweries. Germany 2002, 136, CBMC – The brewers of Europe, 2002, 140, World Bank (IBRD), et al., 1998

The following table shows the range of specific environmental impact valid for modern breweries:

Parameter	Unit	Range
Water consumption	hl water/ hl beer sold	4-10
Wastewater generation	hl water/ hl beer sold	1.3-1.8
COD	Kg/ hl beer sold	0.8-2.5
COD / BOD_5 ratio	-	1.5-1.7
Total suspended solids	Kg/hl beer sold	0.2-0.4

Table26. Wastewater and pollution generated in breweries [CBM – The Brewers of Europe, 2002]

Wastewater production for individual process stages, reported for the German brewing industry, is summarised in table 28:

Department	Specific wastewater volume (m^3/hl beer produced)			
	Measured*		Literature	
	From	*To*	*From*	*To*
Brewhouse/ Cold storage	0.024	0.063	0.010/0.008	0.114/0.050
Fermentation cellar	0.005	0.021	0.0012	0.070
Storage cellar	0.005	0.013	0.0014	0.030
Filtering cellar	0.019	0.059	0.0070	0.090
Bottling cellar	0.036	0.068	0.070	0.280
Cask cellar	0.008	0.037	0.0053	0.067
Miscellaneous	0.020	0.204	-	-
Total Process	**0.117**	**0.465**	**0.1029**	**0.701**

* Measurements by Heidemann, Rosenwinkel and Seyfried (1990 to 1992)

Table28. Specific wastewater production in german breweries (1990-1992)

Further work and expected results

Tasks C. Demonstration and D Evaluation are to be started at this stage. The expected results of such tasks are related to obtain indicators that show the differences between conventional and ozone based CIP operations in terms of water consumption, energy consumption, pollution in wastewaters, and evaluation of cleaning and disinfection efficiency of alternative systems. So finally the potential reduction of the environmental impact of sanitation operations is demonstrated. Consideration of as BAT will be analyzed and the expected environmental benefits are:

- <u>Reduction in water consumption</u>. faster oxidation by ozone should reduce rinse-up times required and final rinse might not be needed.

- Improvement of the cleaning wastewater quality. in terms of COD (mg/l). N (mg/l) and P(mg/l), Chlorides (mg/l), absence of unhealthy chlorine derivatives (THMs, chloramines…) in wastewater of sanitizing operations.
- Reduction of the risk of environmental accidents caused by storing disinfecting chemicals in food factories. Ozone does not need to be stored since it is generated on site.
- Energy savings, ozone is used at lower temperatures.
- Other reducing odour emissions and facilitating biological wastewater treatments

indicators that show the differences between conventional and ozone based CIP operations:

- water consumption vs efficiency in C&D
- energy vs efficiency in C&D
- pollution in wastewaters vs C&D efficiency
- evaluation of C&D efficiency of alternative systems

Conclusion

Sanitation is a key operation within food industries. Environmental data related to cleaning has been collected that confirms that the impact of such operations is significant although the actual practice employed in each particular company plays an important role on the level of pollution discharged. The following conclusions in relation to the environmental performance related to cleaning and disinfection operation may be considered:

- In general, more tan 80% of the water consumed in these sectors is used for cleaning purposes.
- Manual operation of CIP is of more common use than expected. It is clear that great savings in the water consumed might be achieved if automation of CIPs was broadly used.
- Installation of measuring devices and keeping registers of consumption values would lead also to optimise the use of water and chemicals for cleaning and disinfection.
- Last rinse and disinfection solutions are often discharged. Although such waters might be recovered for pre-rinse in most cases ozonation might be a security for maintaining safety conditions of such waters in store until next use.
- Values for different in process cleaning operations have been obtained. Unfortunately data only gives a reference hint on the strength of such wastewaters as manually operated CIPs will make the results rather variable. Peaks in pH (pH =12 and pH = 3) and in conductivity are always produced as a consequence of cleaning cycles in the discharged rinsing waters. High organic load is common too. Ozonation of the rinse water might help to reduce the organic load and the conductivity.
- Segregation of first rinse waters polluted with the product remnants is key to reduce drastically the strength of the wastewaters (alcohol recovery, whey recovery). It has been seen than cleaning with high pressure water reduces drastically the amount of water needed but this is practicable in small or medium sized tanks.
- Care must be taken with disinfection steps as toxic wastewater discharges may be generated. Also it has been seen than overdosing cleaning and/or disinfecting products is a waste of valuable chemicals and makes it necessary much higher quantity of final rinse water to eliminate foam and chemical remnants.
- There is not a pattern for the applied amount of water per unit of tank volume, or the time the cleaning solutions are kept circulating in closed loop.
- Although CIP operations contribute to saving water, energy and chemicals, they still generate large volumes of waste water, which may have a high or low pH due to the use of acid and alkaline cleaning solutions. This is dramatically enhanced when cleaning solutions are not recovered for reuse fact that has been observed in some small companies.
- Badly designed CIP systems and inadequate product removal prior to the start of the CIP cycle cause large quantities of product to enter the cleaning water. This fact, along with loss of products by spillage is of great importance from an environmental point of view because of the extreme organic load transferred to the waste waters.

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. Ongoing tasks should demonstrate the extent in which the potential environmental benefits improve the actual impacts of conventional CIP protocols. Adopting ozone in cleaning and disinfection processes has potential advantages over commonly employed disinfectants. Ozone breaks down quickly into oxygen without leaving undesirable residues. This is an advantage both from the point of view of food safety and to improve the quality of waste waters by avoiding the presence of harmful chlorine compounds. Replacing chemical products with ozone also lowers the concentration of salts and, therefore, the electrical conductivity of discharges. The use of ozone can save water in comparison to other biocides, as it is faster-acting. Additionally, since it does not leave residues it does not require a final rinse to remove any residual disinfectant that might remain in the treated medium. Another advantage is that ozonated water used for disinfection can potentially be re-used for the initial cleaning stages. Waste waters are oxygenated by ozone conversion, so ozone use will improve the performance of aeration tanks and biological waste water treatment processes. This is also an advantage from the point of view of reducing odour generation. Ozone use also provides energy savings as it is normally used at low temperatures. Finally, as it is generated "on the spot", ozone removes the need to store hazardous substances which could give rise to accidents that endanger human and environmental health and safety. Most of this issues need indicators that demonstrate numerically such estimates, a pilot plant to obtain numerical data of conventional versus ozone based cleaning protocols has been designed and constructed.

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