

# DISINFECTION AND DISINFECTION BY-PRODUCTS: A NUISANCE IN DESALINATION TECHNOLOGY<sup>1</sup>

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## ABSTRACT

*To overcome the problem of water scarcity and facilitate social development of the nation, Saudi Arabian Government was unprecedented in pioneering and unparalleled in expanding seawater desalination industry. One of the diverse utilities of desalinated water is its use for drinking and other related domestic purposes. In the latter case, it is obviously of dire importance to ensure a safe water supply. For this reason desalinated water has to be treated with some suitable disinfectant before dispensing it the consumer. Almost all desalination plants in the Kingdom of Saudi Arabia use chlorine as the disinfectant of choice. Most of these plants produce their own chlorinating agent by electrolysis of seawater to generate chlorine, which is allowed to react with co-generated sodium hydroxide to form sodium hypochlorite. This seawater generated sodium hypochlorite, NaOCl (SW), is dosed to product water in the form of crude chlorinating agent contained in the parent seawater matrix. Thus, there is always a fear that the carrier seawater matrix becomes charged with disinfection byproducts, DBPs, which may contaminate product water. The DBPs of concern were, in particular, halo-acetic acids (HAAs) and trihalomethanes (THMs). This fear stems from the fact that seawater matrix contains all the precursors necessary for formation of HAAs and THMs byproducts. Apart from hypo-chlorinating agents, several alternative disinfectants are available. Ozone, chlorine dioxide, chloramines, peroxone, Cu II ion, and UV electromagnetic radiation, are examples of disinfectants considered or evaluated as alternatives for chlorine. Each disinfectant of these has some advantages and some disadvantages. In many cases, however, disadvantages far outweigh the advantages. This paper brushes only briefly over the DBPs of these alternative disinfectants. The main objective of the paper is to review, in some details, the available literature relevant to the formation potential of chlorine generated DBPs, their constituent precursors, and the conditions that promote or suppress their*

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*formation reaction. In fact, there is a mounting literature, published in a large number of international journals, in relation to the topic of chloro-disinfectants and their by-products. Surveying such massive literature indiscriminately in this paper may not be very constructive or recommendable, not only because it may overwhelm the main purpose of the paper, but also because of the fact that the most important aquatic precursors for DBPs formation, i.e. dissolved natural humic, and anthropogenically introduced, organic compounds, are indigenous & site specific to the locality where they belong. Even bromide, the second most important precursor for THMs & HAAS DBPs formation, varies significantly in concentration depending on the local marine environment, or groundwater aquifers, where it occurs. Thus, it was envisaged more appropriate, in relation to these compounds, to focus mainly on home-acquired literature rather than expanding far-out into regional or worldwide literature; except, of course, for brief comparative, or elucidative basic chemical information.*

## **1. INTRODUCTION**

Disinfection is inevitable for seawater desalination processes in order to combat pathogenic microbial growth in product water and also to suppress biofouling of the desalination plant components. Apart from being a mandatory step in the pretreatment sequence, disinfection is an equally important post-treatment step. Not only that, but it may also prove necessary even within the course of the desalination stream. However, disinfectants almost invariably have some problems associated with them. Toxicity of the disinfectant or its by-products (DBPs), cost, stability, potency, ease of handling, etc, are examples of those problems. Although chlorine-derived group of disinfectants possess an almost unbeaten germicidal effect, they are not an exception with respect to associated problems. One major problem of these, is the high toxicity of their disinfection by-products. To date, and over the last century, hypochlorinating agents have been the most popular disinfectants in water treatment. Different forms of hypochlorinating agents which have been most widely used, include chlorine gas, sodium hypochlorite solutions, and calcium hypochloride, all of which are commercially manufactured. In addition to these, some major desalination plants synthesize their own hypochlorite disinfectant on-site. This is usually done by electrolysis either of seawater or brine (Figure 1a & 1.b). However, because raw seawater may contain a myriad of contaminants, there is a fear that some of these contaminants may persist in the generated hypochlorite and, on treatment, find their

way to the product water. Even with other commercial hypochlorinating agents, there is still a possibility that the strongly oxidizing agent, when added to raw seawater reacts with dissolved natural organic matter (NOM) and other oxidizable entities, resulting in undesirable, potentially toxic, chlorinated and unchlorinated organic contaminants which may carry over to product water [1]. These phenomena lead to very tight restrictions on the allowable level chlorine residual in potable water, reducing it to not more than 0.1 – 0.2 mg/L. These low level restrictions had somewhat limited the effectiveness of the disinfectant.

Carry-over of volatile DBP contaminants doesn't constitute a problem in MSF desalination technique due to repeated venting of these compounds during the process. Thus, MSF distillates do not contain more than trace amounts of THMs, if at all. This is a fact that had been verified and confirmed through extensive studies as well as routine monitoring. However, the situation is different in case of SWRO. Using the somewhat hydrophobic membranes e.g. cellulose acetates, SWRO product water may be contaminated with DBPs such as THMs, HAA and the like. In contrast to the situation with MSF, analogous studies regarding DBPs removal by SWRO membranes are very sparse. Even the few available studies, in spite of their importance, are mostly sporadic and incomprehensive. However, a comprehensive project to study formation potential and fate of various DBPs within the course of SWRO and SW NF/RO processes is already in preparation in the chemistry department of the R&D Centre. The project will focus on monitoring the levels, identifying the nature, and tracking the fate of the DBPs and their precursors under varied conditions, varied disinfectants and varied application points. The study is particularly intended to investigate the impact of DBPs on different RO and NF membranes. A follow up study is also in mind pending to be carried out, not only within the SWRO stream, but also beyond the RO permeates to include investigation of post-treatment disinfection impact on storage tanks, in simulated ground water blending, simulated distribution system, and also along transmission lines of RO product water.

## **2. CHEMICAL BEHAVIOUR OF DIFFERENT FORMS OF HYPOCHLORINATING AGENTS**

As a water disinfectant, chlorine can be applied in different forms of hypochlorinating agents. These forms include compressed chlorine gas, and solutions of sodium

hypochlorite and calcium hypochlorite. The latter is usually marketed in solid form (powder or tablets). Chlorine can be obtained commercially for disinfection in any of these three forms or locally generated on site, as mentioned before. Economically, considering a per unit mass of active chlorine cost, calcium hypochlorite is more expensive than the other forms, followed by sodium hypochlorite. The use of liquified chlorine on a large scale is the least expensive, had it not been shrouded with risks of accidental leakage or explosion of the pressurized toxic gas. Chemically, the three commercially available forms of hypochlorinating agents as well as the on-site generated form, are equivalent (eqns. i-iii below). This equivalence is due to the rapid equilibrium established between chlorinating agents and the hydrolysis reaction products of hypochlorite compounds. In fact, this reaction had been reported to reach completion in about 100 ms [2-4].

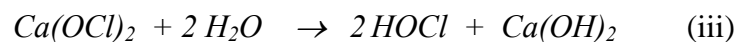
Chlorine gas:



Sodium hypochlorite:

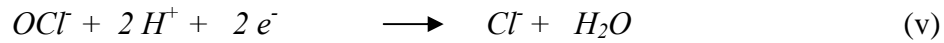


Calcium hypochlorite:



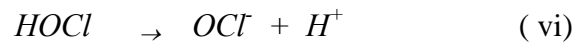
As can be seen from equation (iv) one mole of oxidising elemental chlorine is capable of reacting with two moles of electrons (abstracted from an oxidizable reactant) to form inert chloride. Similarly, equation (v) shows that one mole of oxidising hypochlorite also reacts with two moles of electrons resulting in the reduced form of inert chloride. Hence one mole of hypochlorite is electrochemically equivalent to one mole of molecular chlorine, and may be said to contain 70.91 g of available chlorine (identical to the molecular weight of chlorine) [2]

Thus, application of either of the hypochlorite salts of sodium or calcium in potable water achieves the same results as does chlorine gas,



The active ingredient in all of these cases is the hypochlorite ion which hydrolyses to hypochlorous acid. The extent of the above hydrolysis reactions i.e. the relative amounts of chlorine species formed in water is strongly dependent on pH and also on temperature, ionic strength as well as the total (initial) concentration of chlorine present. Figure (2) illustrates the effect of pH on the relative amounts of the three species chlorine,  $OCl^-$  and  $HOCl$  in water. At 25°C  $HOCl$  is the predominant species between pH 1 and 7.5 whereas  $OCl^-$  is predominant at pH greater than 7.5 [5].

Hypochlorous acid is a weak acid ( $pK_a$  7.5 at 25°C), which dissociates in accordance with equation (vi):



Based on the above  $pK_a$  value and the hypochlorous acid dissociation equilibrium, the relative concentration ratio of hypochlorite to hypochlorous species may be obtained from the following expression at 25°C:

$$\log ([OCl^-]/[HOCl]) = 7.5 - pH \quad (vii)$$

Tables (1.a) & (1.b) show, respectively, the effect of temperature on  $HOCl$  per cent concentration at different pH values and the per cent concentration of  $Cl_2$ ,  $HOCl$ , and  $OCl^-$  at different buffered pH values as a function of initial solution concentration.

It has been postulated that an aqueous chlorine gas solution at pH 2 to 3 will always be somewhat more effective than a solution of sodium hypochlorite at pH 11 to 12 at the immediate vicinity of the application point. This is simply because there is more

active HOCl species at the lower pH range and possibly because of the presence of some extremely active molecular chlorine on account of the low pH of the chlorine gas solution. It is a well known fact that at pH 11 to 12 the HOCl is almost completely dissociated to the ineffective hypochlorite ion [6]. However, though reported as less effective a disinfectant than the hypochlorous molecule, the hypochlorite ion possesses a higher standard potential ( $E^{\circ}_{\text{red}} = 1.64 \text{ v}$ ) than that of the hypochlorous molecule ( $E^{\circ}_{\text{red}} = 1.48 \text{ v}$ ) [5]. The negative charge on the hypochlorite ion has been reported to retard its penetration of the cell wall of a micro-organism. This kinetics related phenomenon may be one reason for the apparent ineffectiveness of the hypochlorite ion.

An empirical correlation between  $\text{pK}_a$  of hypochlorous acid and temperature has been provided as shown belows [7,8]:

$$\ln \text{pK}_a = 3.184 - 0.0583T - 6908/T \quad (\text{viii})$$

Table (2) shows the effect of temperature on the dissociation constant of hypochlorous acid.

Despite the fact that the different forms of commercial and on-site generated hypochlorinating agents are chemically equivalent as far as chlorination products are concerned, they do differ in the side reactions of their end products. The hydrolysis reaction with the hypochlorite raises the pH and alkalinity through generation of hydroxyl groups as sodium hydroxide and calcium hydroxide. On the other hand, addition of chlorine to water reduces the pH and alkalinity by increasing the  $\text{H}^+$  ion concentration (reaction v); whereas addition of calcium hypochlorite contributes further to increase the hardness of the aqueous solution and thus promotes scale formation. In case of on-site generation, the hypochlorite differs in that it is obtained in a solution matrix of a high ionic strength. The pH, and other side effects, take place in accordance with the same reactions illustrating chlorination equivalence of the different hypochlorinators as represented by equations (i), (ii) & (iii), above. These equations *are reproduced below for convenience:*



### 2.1 Available chlorine

The term *Available chlorine* is commercially used to denote the *relative* amount of chlorine present in a chlorine gas or a hypochlorite salt. The concentration of hypochlorite (or any other oxidizing disinfectant) may be expressed as available chlorine by determining the electrochemical equivalent amount of Cl<sub>2</sub> to that compound. The term *free available chlorine* is used to refer to the sum of the concentrations of molecular chlorine (Cl<sub>2</sub>), hypochlorous acid (HOCl), and hypochlorite ion (OCl<sup>-</sup>), each expressed as available chlorine.

## 3. DISINFECTION BY-PRODUCTS OF HYPOCHLORINATION

Disinfection by-products include a large number of organic and some inorganic compound generated as a result of application of disinfectant to different types of water. At the present time, however, there is more concern about a somewhat limited number of classes of organic compounds. These are actually the compounds identified by the United States Environmental Protection Agency (USEPA) as potentially toxic, mutagenic, or carcinogenic compounds. They are included in what became known as the priority list of pollutants. These classes of organic compounds, result mainly from the use of chlorine-derived disinfectants for potable water. They include trihalomethanes (THMs), halogenated acetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), and miscellaneous other chlorinated and brominated organic compounds such as chloral hydrate, chloropicrin (CP), cyanogen chloride and cyanogen bromide (CC and CB). The list also include some inorganic oxohalides like bromate and chlorate. The first two classes of these compounds are the ones that are currently receiving most concern and attention. The potential of formation of these organochlorine compounds, apart from conditions of disinfectant concentration, contact

time, temperature, pH, etc, depends mainly on the concentrations of precursors present. The most important precursors loads are the humic substance which are ubiquitous in natural aquatic reservoirs as dissolved organic carbon. Also, another contribution to the aquatic organic carbon load, is that originating from exudates of different aquatic biota, both fauna and flora. In addition, there is frequently an anthropogenic contribution aquatic organic carbon load through transport of organic pollutants from point or non-point sources, to various locations of water resources. The second most important precursor for formation of these DBP's is the bromide ion. The hypochlorinating agent, along with its disinfection action, oxidises both of these precursors. The humic portion of dissolved aquatic organic carbon constitutes the bulk of the total organic carbon. It consists of a composite mixture of highly refractory non-biodegradable polymeric macro-molecules of highly variable molecular weights. Each of these macromolecules incorporates assortments of different organic moieties and functionalities. As such, they are not suitable for nutrition of micro-organisms. Chlorine disinfectants oxidize these molecules and break them down into simpler assimilable molecules. The products of chlorine oxidation of these organic compounds include both chlorinated and unchlorinated organic derivatives [1]. Chlorine also oxidizes Bromide ions to molecular bromine, which in aqueous solution, behaves in much the same way as molecular chlorine. Analogous to chlorine, bromine equilibrates into hypobromous acid, hypobromite ion and molecular bromine forms. In these forms, it competes with their counter-parts of chlorine species for reaction with organic entities in solution. The result is the formation of a spectrum of volatile and non-volatile chloro-, bromo-, and mixed bromo-chloro- derivatives of organic compounds. THMs and HAAs, are examples of such a spectrum of halogenated products. THMs include bromodichloro- and chlorodibromo- methanes, in addition to chloroform and bromoform; whereas HAAs include monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid and bromochloroacetic acid. These are abbreviated, respectively, as MCAA, DCAA, TCAA, MBAA, DBAA & BCAA. All of these halogenated compounds are considered to be toxic, carcinogenic and/or mutagenic, in addition to being environmentally hostile because of their non-biodegradability and their bio-accumulation capability.

#### **4. DISINFECTANT-DISINFECTION BY-PRODUCTS (D-DBP) RULE**

The Disinfectant-disinfection by-products (D-DBP) Rule addresses complex and interrelated issues relating to disinfectants [9]. The risk of microbial disease outbreaks must be balanced against the risk associated with disinfectants and their by-products. Little is known about the occurrence of most DBPs, and the lack of knowledge regarding treatment effectiveness for DBP control complicates and inhibits regulatory decision-making. For these reasons the rule would be developed in two stages. The regulatory-negotiation (reg-neg) committee had set for stage I maximum contaminant level (MCL) for total trihalomethanes THMs as 0.080 mg/L whereas an MCL for the total of five haloacetic acids (HAA5), was set at 0.060 mg/L. The five HAAs are monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid. Stage I was promulgated in 1996. Stage II, which will reduce the above MCLs for THM's and HAA5 to 0.040 mg/L and 0.030 mg/L respectively. These lower MCL's are scheduled to be effective as of January 2002.

##### **4.1. Hypochlorinating Agents Behaviour**

###### **4.1.1. *Multistage Flash Desalination (MSF) Process***

One of the most comprehensive studies that has been carried out on DBP's in SWCC plants of the eastern district, was sponsored by SWCC, and carried out as early as 1985 in coordination between RDC and RI (then known as the Research Institute and was affiliated to UPM, now KFUPM) on MSF desalination streams of Al-Jubail, Al-Khobar and Al-Khafji plants [10]. In this study, more than 500 samples were collected from almost every stage in the desalination stream and analyzed for THM's and various kinds of DBPs. Sampling locations (Fig's. 3. a, b & c), included the intake bay, chlorinated and unchlorinated intake feed, make-up seawater, brine recycle, brine blow down, desalinated product water, post-lime treatment chlorinated product water, post-storage-tank chlorinated product water, as well as line-transmitted product water up to Riyadh HPT. In addition, several samples of on-site generated sodium hypochlorite, which was then used only by Al-Khobar plant as the chlorinating agents were also analysed. The study focused more emphasis on Al-Khobar (Al-Azizia) and Al-Jubail desalination plants. Within the main desalination streams of the former, starting from the

intake feed to the unchlorinated product water, the study identified three groups of organic compounds at certain stages of both plant streams.

The first group consisted of two of the volatile trihalomethanes, namely, bromoform and chlorodibromomethane. However, these compounds, produced as a result of chlorine reaction with the organic constituents naturally occurring in the water, were detected, in all stages, only at concentrations well below the maximum contaminant level (MCL) set by the United States Environmental Protection Agency (USEPA).

The second group consisted of phthalate esters. These compounds were found in several product and other upstream water samples. Phthalate esters are extensively used as plasticizer in the plastic industry and also in the preparation of certain types of antifoaming agents. Although it is most likely that they might have emanated from one or more of these sources, the possibility of their formation as nonchlorinated by-products of chlorine oxidation of NOM, may not be ruled out completely. The study identified two phthalate esters. These were benzyl butyl phthalate and bis(2-ethylhexyl) phthalate.

The third group comprised several chlorinated organic compounds. The source of these compounds were found to be the sodium hypochlorite used for chlorination of seawater. However these compounds which were detectable in seawater, were completely absent from product water. Thus, they were not able to escape and carry over into product water indicating that MSF is a very effective desalinating technique in removal of both volatile and nonvolatile organic contaminants that may form in the intake seawater.

Furthermore, the study spotted four additional halogenated organic compounds which were shown to have formed as a result of product water chlorination. The four organic contaminants were identified to be: a) 2-chlorocyclohexanol b) 2-bromocyclohexanol c) 1-bromo,2-chlorocyclohexane, d) 1,2-dichlorocyclohexane

Although, toxicity data of this last group of compounds are not available in the literature, yet on structural basis, they may be anticipated to pose health hazards in a way similar to other halogenated hydrocarbon. The report stressed that the concentration of these compounds in Al-Azizia treated water were at all times higher

than that of Al-Jubail water. They attributed this phenomenon to the fact that sodium hypochlorite was used for disinfecting the water at Al-Azizia plant, while the disinfectant then used in Al-Jubail plant was chlorine gas [10]. Based on their experimental results, the on-site generated sodium hypochlorite was found to contain many halogenated organic compounds in addition to the four cyclohexane derivatives. These latter findings were also published by Fayad and Iqbal elsewhere [11]. However, Jolley et. al.[12] discussed the presence of these latter compounds and considered them to be, most probably; artifacts attributable to cyclohexene preservative in the methylene chloride used in the analytical process. Obviously, Jolley's interpretation doesn't seem to be founded since these compounds neither showed up in the extracts of the sampling stages preceding the product water chlorination stage, nor did they show up in the extract of analytical reagent grade sodium hypochlorite; eventhough the extractant used in all of these cases was the same methylene chloride. Moreover, in another study, Kutty et. al. [13], identified, among several other compounds, two of the above four compounds (namely c & d) in the hypochlorite header of all of Al-Jubail, Al-Khobar and Al-Khafji plants. In the latter plant although compound (d) was identified alone but it was among several related compounds e.g. monochlorocyclohexane. These findings of Kutty et. al. support the results of the RI studies. [10,11] However, none of these cyclohexane related compounds were identified in chlorinated product water in any sampling station of the latter study. In the study of Kutty et. al., bromoform was the only THM which was common to all of the chlorinated seawater samples, as well as in the hypochlorite headers of all of the three stations as well. With the exception of Al-Khafji, traces of bromoform were also spotted in the chlorinated product water of Al-Jubail and Al-Khobar. However in Al-Khafji plant, low traces of bromoform were observed in both chlorinated and unchlorinated product water.

The second group of phthalate esters (PE's) of the RI investigation, were identified in Kutty's study, only in chlorinated feed seawater of Al-Khobar (dibutyl PE) and Al-Khafji plants (butyl dimethyl-hexyl PE) but not in Al-Jubail. Moreover, in contrast to what had been revealed in Fayad and Iqbal study, these compounds were completely absent from product water. They were also absent from the hypochlorite solution headers of the three plants according to Kutty et. al. It should be noted here, that at the time of Kutty's study, all of the three plants had on-site chlorine producing units installed.

#### ***4.1.2 Sea Water Reverse Osmosis Desalination (SWRO) Process***

Apart from some sporadic investigations here and there, very little systematic studies were reported in the literature with respect to DBP's formation potential, and precursors behaviour, in different stages of SWRO membrane processes. This is probably because in seawater reverse osmosis processes, rejection of DBPs, as exemplified by THMs behaviour, differs greatly with the nature, type and operation conditions of membranes used. In a Japanese study along the coast of Japan, a typical seawater, taken from a depth of 3 m, was treated with chlorine as sodium hypochlorite and allowed a 2–4 hours contact time [14]. When this prechlorinated water was used as feed for a cellulose triacetate membrane, the THM's concentration in the feed water was 15–25 µg/L. As the feed seawater contained finite amounts of organic matter and relatively high levels of bromide, bromoform was the main THM generated with the addition of chlorine, as expected. Surprisingly, the THM's concentration in the permeate was 1.2–1.5 as much as that in the feed water. Thus, THM's were not only unremoved but, on the contrary, their concentration was even enriched on the permeate side of the membrane. On the other hand, when polyamide membranes were used instead, after dechlorinating the feed with SBS, THM's concentration in the permeate dropped to 0.1–0.2 of that of the feed water. That is, about 80–90% of the THM's were separated by the polyamide membranes and withheld in the brine side of the membrane. These THM's were neither found retained within, nor adsorbed to, the surface of, the polyamide membrane [14].

Alternatively, when chloramine was used as the disinfectant, THMs were scarcely generated. In the chloramine-treated feed water the THM concentration levels were found to be sometimes less than a microgram per liter (<1 µg/L), whereas their corresponding concentrations in the permeate of the cellulose triacetate membrane were obtained at higher level of about a microgram per liter (~1 µg/L), [15]. Precursors levels in the feed seawater were reported [14] to be 69 mg/L for Br<sup>-</sup> ion, 0.5 mg/L as COD, and a chlorine residual of 0.3 mg/L for cellulose triacetate versus 0 mg/L for polyamide membrane (residual of 0.3 mg/L SBS dechlorinated ahead of cartridge filter). However, for RO permeate, the corresponding values of THM contaminant levels were not reported; probably indicating low concentration values, since their slots were left vacant in the report.

The above noted behaviour of THMs towards enriching the permeate side of cellulose triacetate membrane, probably find support in the studies carried out at Yuma Desalination Test facility, where it quoted that THMs were present in RO feed, and that they are considered candidate RO membrane foulants [16].

Data obtained from other representative studies carried out in the R&D Center [17,18] had consistently showed extremely low levels of these organo-chlorine by-products. Similarly, data of years of periodic monitoring of DBP levels in MSF and RO product water from plants in the Kingdom, carried out by the chemical laboratories of the R&D Center, had also consistently confirmed those frequently undetectable organo-chlorine DBP levels. Representative samples of data obtained from the above mentioned R&D Center studies together with sample data of periodic monitoring of DBPs levels in MSF and RO product water of some plants in the Kingdom, are shown, respectively for THMs and HAAs, in tables (3) & (4).

#### ***4.2. Alternative Disinfectants & DBPs***

There is a large number of disinfectants alternative to chlorine. These alternatives include ozone, chlorine dioxide, chloramines, peroxone (hydrogen peroxide and ozone),  $\text{CuSO}_4$  salt, UV irradiation, to name Just a few. Each disinfectant of these has, to a variable extent, some merits and some limitations. In some cases the limitations outweigh the merits. Ozone have been in use for several decades in Europe, the late USSR republics and USA. The inadequacy of ozone was mainly the interference by manganese and iron and, particularly, excessive formation of bromate and also bromoform in presence of high levels of bromide. All of these drawbacks are in addition to difficulties in operating and maintaining the associated ozone generating equipments. These factors, coupled with lower cost, greater flexibility, and better reliability of chlorination versus ozonation, contributed to the somewhat limited use of ozone worldwide. In terms of DBP's, the use of ozone leads to excessive formation of bromate oxohalide ion. This has been assigned an MCL of only 10 ppb by the USEPA.

Kutty And Al-Jarrah [19] considered the advantages and limitations of four disinfectants that they considered relatively safe for use with drinking water. Apart from chlorine, these disinfectants included chloramine, chlorine dioxide and ozone. These authors, and others, considered that although ozone is a very strong oxidizing and disinfecting agent, producing little THM's, removing taste and odour from treated water, its main drawbacks are high capital cost, incapability of deep penetration, as well as its inability to impart a residual protection against microbial aftergrowth in distribution systems [19,20,21]. Fig. (4) shows an example of experimental UV unit installed downstream of an NF/RO train in Al-Jubail pilot plant [21].

However, Kutty et. al. [22] concluded that both ozone and chloramine as alternatives to chlorine, may not be helpful in reducing THMs in bromide rich seawater. They reported that even chloramine which normally produces very low concentration of THMs in surface water samples, was found to generate substantial amounts of THMs in the presence of high bromine in the source water. The study also revealed that MSF distillates do not contain appreciable amounts of THMs, but inferred that SWRO using less hydrophilic membranes such as cellulose triacetate, product permeate may be contaminated with THMs. The absence of THMs in MSF distillate was attributed to losses of both THMs and inorganics present in seawater during vacuum distillation [22]. Similarly, concentration levels of HAAs monitored in product water of Al-Jubail MSF plants were found to range very much below MCL of 60 ppb [17]. These much lower HAAs levels, compared to their counterparts normally spotted in raw seawater, are apparently due to significant loss of small halogenated and nonhalogenated organics during flash distillation [1,23].

Chlorine dioxide,  $\text{ClO}_2$ , is a strong oxidizing which reacts rapidly with naturally occurring oxidizable organic and inorganic species. As a result it become reduced to the more or less undesirable by-products of chlorate,  $\text{ClO}_3^-$ , chlorite,  $\text{ClO}_2^-$ , and chloride,  $\text{Cl}^-$ . In addition, like ozone, it oxidizes bromide when present generating bromine,  $\text{Br}_2$ , and bromate ion,  $\text{BrO}_3^-$ . Furthermore, in presence of humic material, it forms THMs (particularly bromoform) and HAAs [24].

Some heavy metal ions have also been used as disinfectants. Exmples include copper and silver ions. Nada et. al. reported on the application of copper sulfate as a

disinfectant in a regional satellite SWCC plant [25]. The application of silver as a disinfectant, which is claimed to be a success, was also reported in the literature [1,26]. The claimed success of silver lied in the effective disinfection achieved at a concentration level of 10, which is well below the 80 ppb MCL limit of USEPA for  $\text{Ag}^+$ .

The R&D Center had a long history of investigations regarding DBPs. This lead to an accumulated wealth of information and acquired experience. Comparative studies of different disinfectant levels, different precursors levels, different conditions affecting formation potential and other related optimization studies, were all carried out in the Center. This is reflected in the standadization, optimization and perfection of chemical methodologies pertinent to DBPs determinations at ultra trace levels, and frequently, in complex and difficult matrices. Research achievements as regards to DBPs can also be observed in several development of creative modifications of known chemical methods to suit of the otherwise cumbersome chemical analysis, or in adapting already existing methods for some locally unique analytical situations.

Investigation of DBP loads were occasionally carried out at various points in desalination streams, in plants situated at various environmentally different sites. These included testing various possibilities of dose application points in relation to various sequential pre- and post-treatment stages. The results obtained from these studies further evolved into an adminstrative decision of weekly and mounthly routine monitoring of these DBP's, so as to ensure continued safety of the product water. The data that will eventually accumulate can, in the long run, serve as a useful database for evaluation, and decision making processes relating to the performance of relevant disinfecants.

## **5. CONCLUSION**

1. Chlorination, at least at the present time, and possibly for quite sometime to come, remains the disinfection practice of choice. Different forms of hypochlorinating agent appear, on the whole, to be adequate for doing the job in most cases, despite minor previlages of some of them versus the others in certain applications.

2. None of the numerous alternatives seems to be a candidate possessing the desirable universal properties of cost, efficiency, etc. to currently replace chlorine.
3. The nuisance is that chlorine itself is by no means the ideal disinfectant, and efforts must continue relentlessly in search of an ideal, *or close to ideal*, alternative; despite the general rule of thumb that stronger oxidants produce more disinfection by-products.

## **6. RECOMMENDATIONS**

1. Although, a relatively massive work have been carried out on DBPs in MSF desalination processes, few studies appear to have been carried out with respect to their analog SWRO processes. Further detailed studies in this respected are recommended.
2. Also, the membrane industry is required to develop new chlorine-resistant membranes of equal, or even better performance levels and in suitable configurations, to replace current membranes that are sensitive to chlorine disinfectants.
3. One of the recommendations that the RI study forwarded and sounds logical, was elimination of the chlorination step of product water preceding blending. They justified this as that the step elevates the level of DBPs unnecessarily since it will, anyway, be chlorinated again after blending.

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**Table 1a. Effect of temperature on HOCl % concentration at different pH**

<i>pH</i>	<i>Percent HOCl</i>						
	<i>0°C</i>	<i>5°C</i>	<i>10°C</i>	<i>15°C</i>	<i>20°C</i>	<i>25°C</i>	<i>30°C</i>
5.0	99.85	99.82	99.80	99.79	99.74	99.71	99.68
5.5	99.53	99.45	99.36	99.27	99.18	99.09	99.00
6.0	98.53	98.28	98.00	97.73	97.45	97.18	96.92
6.1	98.16	97.84	97.50	97.16	96.82	96.48	96.15
6.2	97.69	97.29	96.88	96.45	96.02	95.60	95.20
6.3	97.11	96.62	96.10	95.57	95.05	94.53	94.04
6.4	96.39	95.78	95.14	94.49	93.84	93.21	92.61
6.5	95.50	94.75	93.96	93.16	92.37	91.60	90.87
6.6	94.40	93.47	92.51	91.54	90.58	89.65	88.78
6.7	93.05	91.92	90.75	89.58	88.43	87.32	86.27
6.8	91.41	90.03	88.63	87.23	85.85	84.54	83.31
6.9	89.42	87.77	86.10	84.43	82.82	81.29	79.86
7.0	87.04	85.08	83.10	81.16	79.29	77.53	75.90
7.1	84.22	81.92	79.63	77.39	75.26	73.27	71.44
7.2	80.91	78.25	75.64	73.11	70.73	68.52	66.52
7.3	77.10	74.08	71.15	68.35	65.75	63.36	61.22
7.4	72.78	69.42	66.20	63.18	60.39	57.87	55.63
7.5	67.99	64.33	60.88	57.68	54.77	52.18	49.90
7.6	62.79	58.89	55.27	51.98	49.03	46.43	44.17
7.7	57.27	53.23	49.54	46.23	43.32	40.77	38.59
7.8	51.57	47.48	43.81	40.58	37.77	35.35	33.30
7.9	45.82	41.79	38.25	35.17	32.53	30.28	28.39
8.0	40.18	36.32	32.98	30.12	27.69	25.65	23.95
8.1	34.79	31.18	28.10	25.50	23.32	21.51	20.01
8.2	29.77	26.46	23.69	21.38	19.46	17.88	16.58
8.3	25.19	22.23	19.78	17.76	16.10	14.74	13.63
8.4	21.10	18.50	16.38	14.64	13.23	12.07	11.14
8.5	17.52	15.28	13.46	11.99	10.80	9.84	9.06
8.6	14.44	12.53	11.00	9.77	8.77	7.97	7.33
8.7	11.82	10.22	8.94	7.92	7.10	6.44	5.91
8.8	9.62	8.29	7.23	6.39	5.72	5.18	4.75
8.9	7.80	6.70	5.83	5.15	4.60	4.16	3.81
9.0	6.29	5.39	4.69	4.13	3.69	3.33	3.05
9.5	2.08	1.77	1.53	1.34	1.19	1.08	0.98
10.0	0.67	0.57	0.49	0.43	0.38	0.34	0.31
10.5	0.21	0.18	0.15	0.14	0.12	0.11	0.10
11.0	0.07	0.06	0.05	0.04	0.04	0.03	0.03
11.5	0.02	0.02	0.015	0.013	0.012	0.01	0.01
11.7	0.01	0.01	0.01	0.01	0.007	0.007	0.006

\*Computer printout courtesy D. S. Cherry, N.C. State Univ., Raleigh, N.C.

**Table 1b. Percent Molecular Chlorine, Hypochlorous Acid, and OCl-ion in a Water -Solution Buffered from pH 6 – 9 at 20 °C**

<b>Solution Concentration (mg/liter)</b>									
	<b>5000</b>			<b>7000</b>			<b>10000</b>		
<b>pH</b>	<b>Cl<sub>2</sub></b>	<b>HOCl</b>	<b>OCl<sup>-</sup></b>	<b>Cl<sub>2</sub></b>	<b>HOCl</b>	<b>OCl<sup>-</sup></b>	<b>Cl<sub>2</sub></b>	<b>HOCl</b>	<b>OCl<sup>-</sup></b>
6.5	.0063	92.28	7.71	.0088	92.28	7.71	.0126	92.28	7.71
7.0	.0017	79.10	20.89	.0024	79.10	20.89	.0034	79.10	20.89
7.5	.0004	54.84	45.51	.0005	54.49	49.51	.0007	54.49	45.51
8.0	.0001	27.46	72.54	.0001	27.46	72.54	.0001	27.46	72.54
8.5	.0000	10.69	89.31	.0000	10.69	89.30	.0000	10.69	89.30
9.0	.0000	3.65	96.35	.0000	3.65	96.35	.0000	3.65	96.35

**Table 2. Effect of temperature on dissociation constant of hypochlorous acid**

Temperature (°C)	0	5	10	15	20	25	30
K <sub>i</sub> x 10 <sup>10-8</sup> (moles/liter)	1.488	1.753	2.032	2.320	2.621	2.898	3.175

Table 3a. Individual and total THMs in blended potable water samples (µg/L)

SL	CHCl <sub>3</sub>		CHBrCl <sub>2</sub>		CHBr <sub>2</sub> Cl		CHBr <sub>3</sub>		Tot. THM
	Avg	Range	Avg	Range	Avg	Range	Avg	Range	Avg
1.	0.02	0-0.07	0.36	0-0.5	0.76	.7-0.8	2.42	2.4-2.5	3.56
2.	0.03	0-0.06	0.31	.3-0.4	0.86	.8-0.9	1.89	1.8-2.	3.08
3.	0.01	0-0.01	0.36	0-0.48	0.86	0-1	4.66	0-5.9	5.89
4.	0.02	0-0.05	0.29	.2-0.3	0.99	.9-1.1	7.2	5.6-8.5	8.52
5.	0.02	0-0.04	0.35	.3-.47	1.4	1.-1.9	9.1	7.8-9.7	10.8
6.	0.01	0-0.03	0.25	.2-.28	1.07	.7-1.22	8.54	7.7-9.7	9.8
7.	0	-	0.29	.25-.3	1.32	1.1-1.5	10.67	9.-12.	12.3
8.	0.24	.060.92	0.41	.1-0.74	1	.8-1.14	1.69	1.5-1.7	3.3
9.	0.45	0-0.9	0.82	.75-0.9	0.9	.86-.92	1.77	1.6-2.	3.9
10	0	-	1.51	-	1.63	-	2.3	-	5.4
11	0.03	0-0.09	0.46	.4-0.5	1.31	1.2-1.4	2.31	2.-2.5	4.1
12	0.03	0-0.1	0.44	.39-.5	1.3	1.2-1.4	2.29	2.1-2.5	4.06
13	0.04	0-0.1	0.42	.34-0.5	1.28	1.2-1.4	2.42	2.3-2.7	4.16

SL= Sampling Locations - Avg: Average

1=Jubail BS#1, 2=Jubail #2, 3=Jubail BS#3, 4 = Khobar BS, 5 = Dammam BS  
 6=Qatif BS, 7= Rahima, 8 = Khafji T#1, 9=Khafji#2, 10=Khafji City Tank  
 11= Riyadh TG-1, 12= Riyadh TG-2, 13=Riyadh TG-3

Table 3b. THM levels in some SWCC plants

S.No	Chemical Name	Unit	MPL	Sample Name			
				Shuqeaqe-1 (Akka)	Shuqeaqe-2 (Apha)	Farasan	Albirk
1	Chloroform	(ug/L)	200	ND	ND	ND	ND
2	Dichlorobormomethane	(ug/L)	60	0.2	0.2	0.3	1.6
3	Dibromochloromethane	(ug/L)	100	0.8	0.7	1.5	0.4
4	Bromoform	(ug/L)	100	1.7	1.4	12.4	6.5
5	TOTAL (THMs)	(ug/L)	*	2.7	2.3	14.2	8.5

MPL : Maximum permissible limit

ND : Not Detected (Less than 0.1 ppb)

\* Note:

The sum of the ratios of the concentration of each THM to its respective guidelines value should not exceed1.

**Table 4. Individual and total THMs in chlorinated well water used for Blending (µg/L)**

<b>Sampling location</b>	<b>CHCl<sub>3</sub></b>	<b>CHBrCl<sub>2</sub></b>	<b>CHBr<sub>2</sub>Cl</b>	<b>CHBr<sub>3</sub></b>	<b>Total THM</b>
<b><u>Al-Jubail Area</u></b>					
BS#1 WWST (a)	0.91	0.15	0.11	0.77	1.94
BS#2WWST	0.50	0.16	0.28	1.97	2.90
BS#3WWST	0.71	0.16	0.09	0.50	1.46
<b><u>Al-Khobar Area</u></b>					
Fowzia	1.62	0.32	0.41	2.92	5.27
Aqrabia (W)	1.84	0.41	1.12	6.17	9.54
Aqrvia (E)	1.42	0.96	0.80	7.39	10.57
Tuqba (E)	1.27	0.34	0.40	5.60	7.61
Tuqba(W)	1.44	0.49	0.83	7.17	9.93
S.pmp station	1.08	0.27	0.64	4.75	6.74
N. pump station	1.27	0.32	1.25	8.13	10.97
Bandaria	1.17	0.29	0.61	5.76	7.83
Green belt	2.18	0.30	0.46	4.71	7.65
Al-Khobar tank	1.85	0.26	0.35	4.50	6.96
Oneza	1.94	0.18	0.76	16.41	19.29
Al-Saudia	1.28	0.26	0.19	3.74	5.47
Al-Raka	1.154	0.15	0.31	8.59	10.59
<b><u>Dammam Area</u></b>					
Well No. 78	4.66	0.0	0.33	3.27	8.26
Well No. 37	2.40	0.0	0.21	1.44	4.05
Well No. 76	2.84	0.0	0.93	5.22	8.99
Well No.91	3.51	0.0	0.07	2.65	6.23
Al-Jameen	4.55	0.16	4.16	13.60	22.47
Dammam WWS	0.0	1.02	3.51	11.10	15.62
Qatif WWST	0.0	0.0	0.02	0.18	0.20
Rahima	0.0	0.0	0.40	5.50	5.90
<b><u>Riyadh</u></b>					
HPT composite	0.03	0.53	1.14	2.98	4.68
Wasia composite	2.36	0.42	0.60	6.30	9.68

(a) WWST = Well water storage tank

From Ref. 18

**Table 5. Analysis of water samples for Haloacetic acid from Al-Jubail plant**

HAAs	Product Water		Product water after lime CO <sub>2</sub> treatment		Blended water		Seawater*	
	Range (ppb)	Mean (ppb)	Range (ppb)	Mean (ppb)	Range (ppb)	Mean (ppb)	Range (ppb)	Mean (ppb)
CAA	ND	ND	ND	ND	ND	ND	ND	ND
BAA	ND	ND	ND	ND	ND	ND	ND to 3.1	1.1
BCAA	ND to 2	0.6	ND to 2.0	0.5	ND to 1.5	0.5	1.4 to 5.3	2.0
TCAA	ND to 3	0.8	ND to 2.6	0.8	ND to 2.1	0.7	1.6 to 2.6	2.1
BCAA	ND to 0.5	0.15	ND to 0.8	0.2	1.0 to 1.5	1.2	ND to 11	1.8
DBAA	ND	ND	ND	ND	ND	ND	ND	ND
Total HAA		1.55		1.5		2.4		7.0

\* R-Cl<sub>2</sub> – 0.1 ppm  
from Ref. 17.

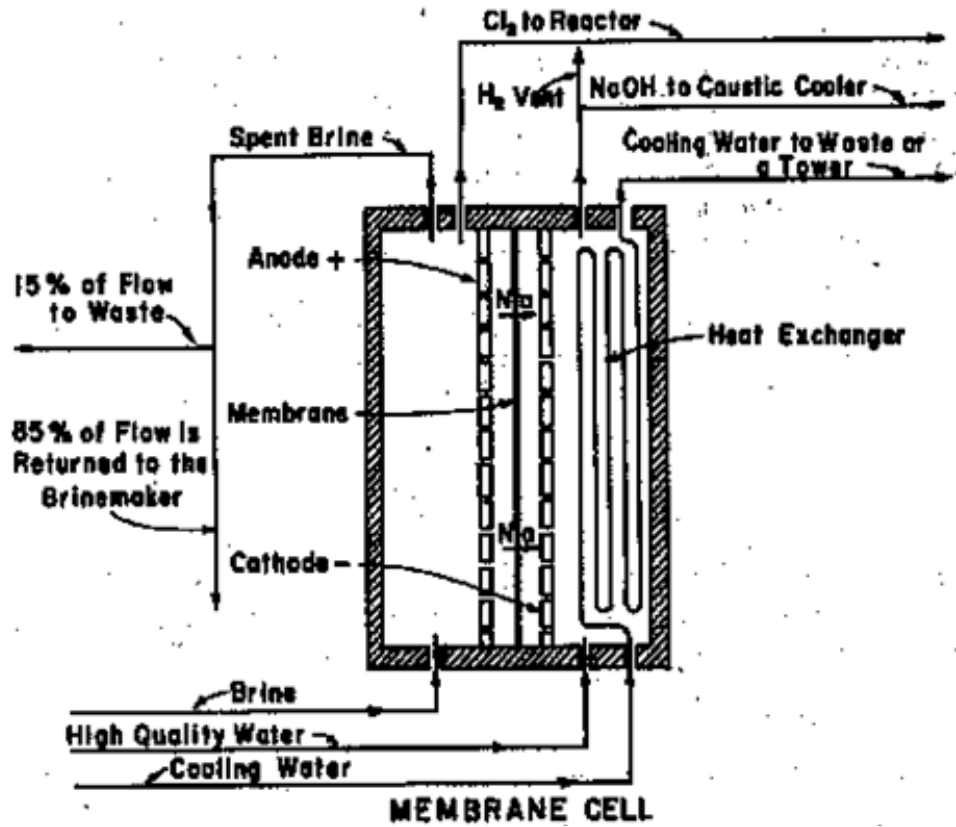


Figure 1a. Cloromat membrane cell with expanded electrodes

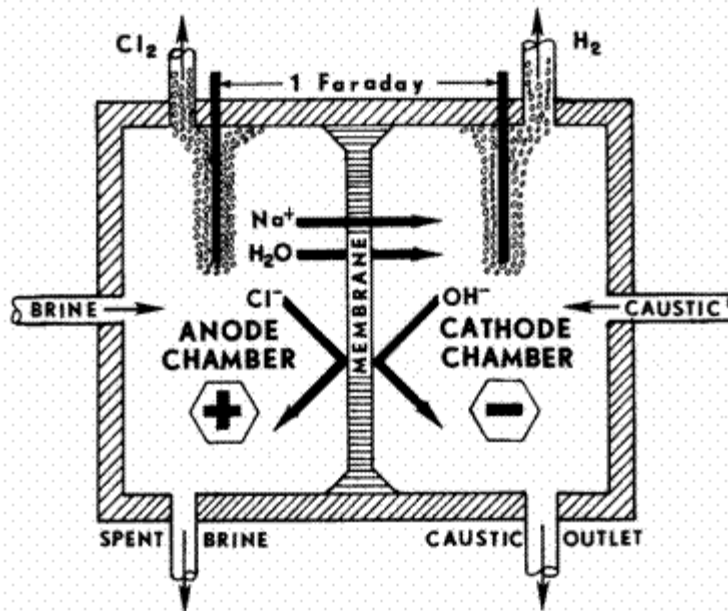


Figure 1b. The ideal membrane cell

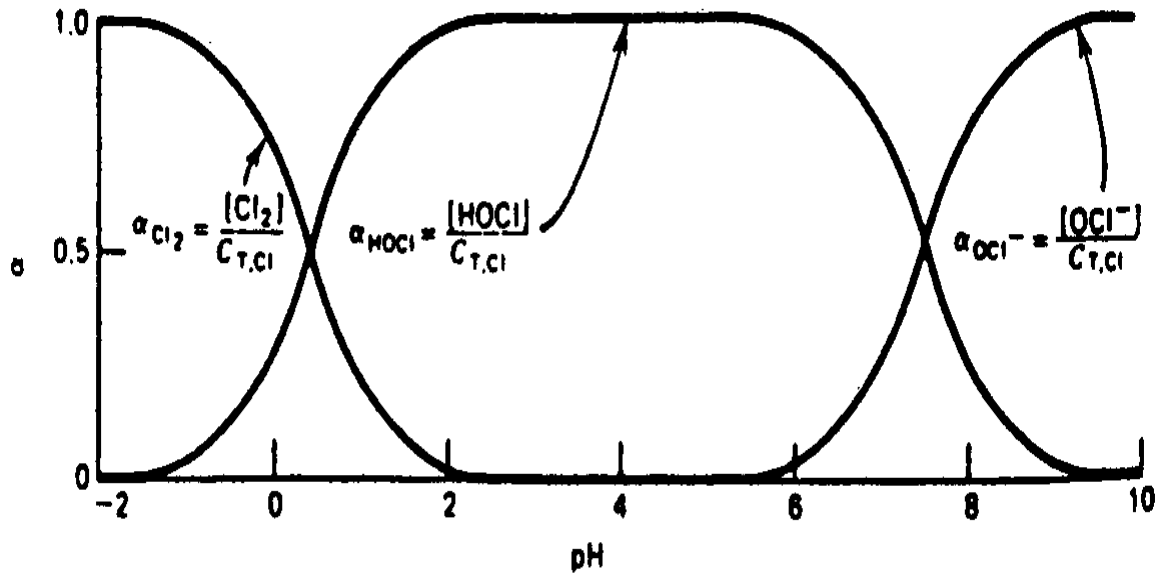


Figure 2. Distribution diagram for molecular chlorine, hypochlorous acid, and hypochlorite ion in water as a function of pH ( $[Cl^-]=10^{-3}M$ ). (Source: Snoeyink and Jenkins, 1980)

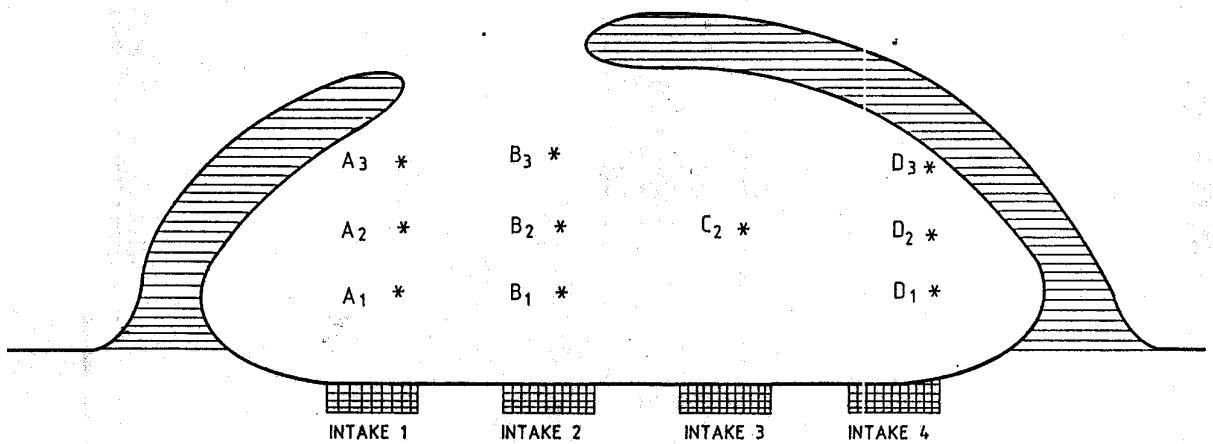


Figure 3a. Schematic diagram showing the sampling locations in Al-Jubail desalination plant intake basin

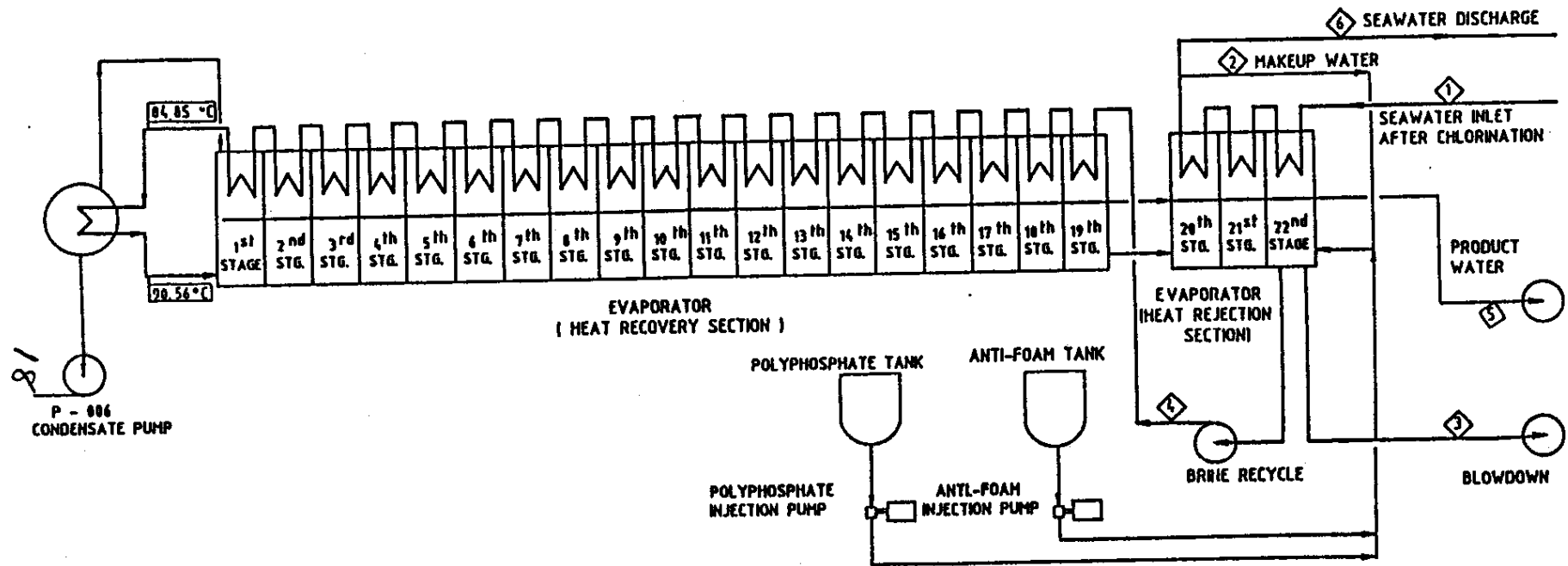


Figure 3b. Schematic diagram of a MSF desalination Plant showing the sampling locations  $\diamond$  1to 5

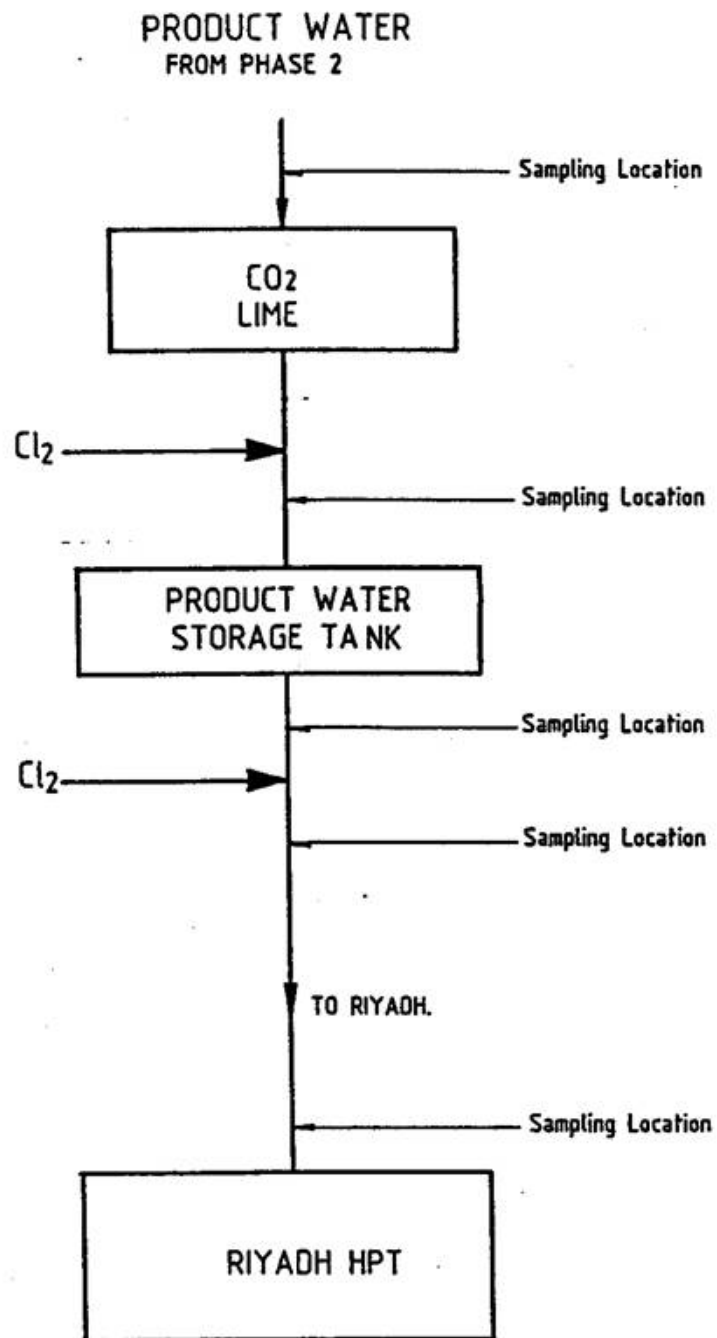
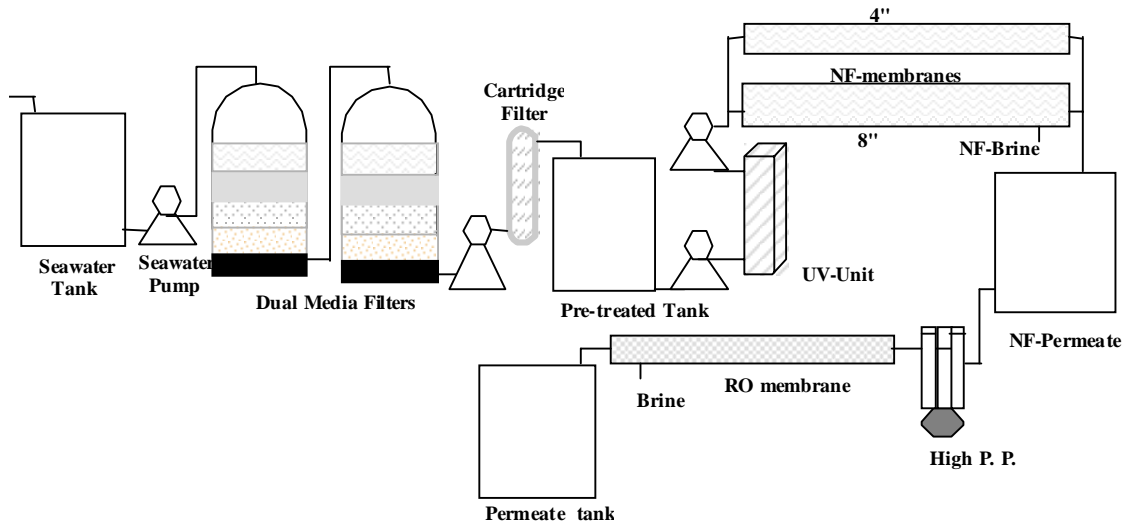


Figure 3c. Flow diagram showing sampling locations of desalination product water



**Figure 4. Applying UV-radiation at RSW Inlet and Before NF Membrane (from Ref. 21)**