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FATE AND CONTROL OF BLISTERING CHEMICAL WARFARE AGENTS IN KUWAIT'S DESALINATION INDUSTRY

Hosny K. Khordagui[a]

Kuwait, as most of the other states located along the Western shores of the Arabian Gulf, relies upon the Gulf as its main drinking water resource via desalination. In case of seawater contamination with blistering chemical warfare agents, traces of the agents and/or degradation products in the finished water might pose a serious health hazard. The objective of the present review is to study the potential contamination, transport, fate, effect and control of blistering chemical warfare agents (CWAs), in the Kuwaiti desalination industry. In general, all the environmental factors involved in the aquatic degradation of CWAs in Kuwait marine environment except for the high salinity in case of blistering agents such as sulphur mustard, are in favor of a fast degradation process. In case of massive releases of CWAs near the Kuwaiti shorelines, turbulence resulting from tidal cycles and high temperature will affect the dissolution process and extend the toxicity of the insoluble agent. Post- and pre-chlorination during the course of seawater desalination will catalyze and significantly accelerate the hydrolysis processes of the CWAs. The heat exerted on CWAs during the power generation-desalination processes is not expected to thermally decompose them. However, the steam heat will augment the agent's rate of hydrolysis with subsequent acceleration in their rate of detoxification. Conventional pretreatment of feed seawater for reverse-osmosis desalination is theoretically capable of reducing the concentration of CWAs by coprecipitation and adsorption on flocs formed during coagulation. Prechlorination and prolonged detention time in pretreatment units will simultaneously promote hydrolysis reactions.

INTRODUCTION

Kuwait, as most of the other states located along the Western shores of the Arabian Gulf, relies upon the Gulf water as its main water resource. This nearly exclusive dependence on seawater as a prime source of potable water

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[a] Ph.D., Regional Advisor on Environment, United Nations Economic and Social Commission for West Asia, Amman, Jordan.

via desalination should never be jeopardized by pollution. The unverified use of certain blistering Chemical Warfare Agents (CWAs) during the Iran-Iraq war,[1] followed by the Iraqi threat of using CWAs against allied forces during Kuwait liberation, has triggered scientific interest on the probable fate and effect of these agents on the desalination industries in Kuwait. The contamination of the feed water will obviously lead to the transport of these potent chemicals to the produced finished water through the desalination processes. Such a contamination might pose a serious hazard to the desalinated drinking water of consumers. In case of a massive release to the marine environment, the main potential target is most likely to be the intakes of power desalination facilities located along the Gulf's shorelines. The basic objective of such an assault would be the contamination of seawater to render it toxic and deny the country of its sole drinking water supply. Other less likely objectives of a CWA assault would be the destruction of marine ecology, and /or the alteration of industrial operations located near the shorelines.

In the present review paper, factors that are known to affect the degradation of CWAs (such as the seawater desalination processes in use, feedwater characteristics and other local and regional environmental conditions) are considered. The main objectives of the review are as follows:

- To envision the most likely scenarios of contamination of seawater at the intakes of Desalination Plants (DP) in Kuwait.
- To assess the likelihood of contamination of desalinated drinking waters with CWAs.
- To review the general fate of blistering CWAs in typical marine environments.
- To project the impact of the unique seawater characteristics and other marine environmental conditions in Kuwait on the fate of CWAs, and in particular, in the vicinity of the DP intakes.
- To review the impact of desalination operation on the chemical nature and integrity of the CWAs of concern.
- To examine the efficiency of desalination on the removal, degradation and/ or detoxification of blistering CWAs of interest.
- To suggest control measures for the minimization of hazards.
- To define the areas of research needed to understand, coordinate, manage and control the hazards associated with seawater contamination with CWAs at the DP intakes in Kuwait.

The potential threat of blistering CWAs to the DPs in Kuwait can be chiefly realized through one or more of the following means:

- Accidental release of the agents or their precursors during loading, unloading, shipping and transportation in the Gulf region.
- Drifting and precipitation of blistering agents from targeted areas during military operations.
- Deliberate disposal of CWA shipments in the Gulf to avoid detection by international inspectors seeking to locate weapons of mass destruction.
- Potential disposal of CWA stock by sinking it in the Gulf.
- The intentional massive releases of CWAs by enemies in conflict.

The selection of the blistering CWAs to be considered in the present review was chiefly based on their history of utilization, prevalence, potency, and confirmed possession by countries in the region.[2,3]

At present, blistering CWAs such as sulfur mustard (bis 2-chloroethyl sulfide) known as (HD), and nitrogen mustard such as (tris 2-chloroethyl amine) known as (HN-3 agent), (N-methyl-2-2'-dichlorodiethylamine) known as (HN-2 agent), and (2,2'-dichlorotriethylamine) known as (HN-1 agent) are considered among the most important lethal agents currently available in the military arsenals of countries in the area and ready for potential application in the region.[4,5] According to Lindesten and Schmitt, HD still remains the blistering CWA of choice.[6]

The Maximum Permissible Concentration (MPC) of blistering CWAs in drinking water is important to determine the suitability of the water for human consumption and use. MPC is also of important consideration in evaluating water decontamination procedures. According to Lindesten and Schmitt, the MPC for blistering CWAs in drinking water was officially fixed in SOLOG (Standardization of certain aspects of Operations and LOGistics) agreement 125 by the quadripartite nations (U.S.A., U.K., Canada, and Australia) at 2.0 mg/l for sulfur and nitrogen blistering agents.[7]

POTENTIAL BREAKTHROUGH OF BLISTERING CWAs INTO DESALINATED WATERS

The desalination process used in Kuwait is Multiple-stages Flash Distillation (MFD) technology. In this process and in accord with World Health Organization (WHO)-recommended salt content, underground brackish water is blended at an average ratio of 1:10 with distilled water.[8] In MFD, each evaporator set consists of a number of vessels in which the seawater is successively evaporated. The seawater is pumped through a sequence of heat exchanger in which its temperature is progressively raised, by condensation of steam produced in corresponding flash chambers, to a temperature of 80 to 100°C. After being heated, typically to 90–120°C, by an external source of steam, the seawater is flashed consecutively down through a number of stages, containing the heat exchanger, where its vapor pressure is progressively reduced. Vacuum is applied to the flash chambers by steam ejectors to maintain the required fall in vapor pressure through the evaporator. In addition to the MFD process, a very limited amount (1000 m^3/day) of desalinated seawater is being generated on an experimental basis through Reverse Osmosis (RO). In RO, seawater on one side of a semi-permeable membrane is subjected to a pressure higher than its natural osmotic pressure, the direction of the flow is reversed and pure water will diffuse through the membrane leaving behind a more salty seawater (brine).

In Thermal Desalination

Based on the volatility, latent heat of vaporization and decomposition temperature of the CWAs and depending on the MFD operating temperature and pressure, the CWA will be subject to one or more of the following simultaneous processes: (1) A fraction of the agent will thermally decompose and breakdown into other substances of similar or lower toxicity; (2) another fraction will be vented to the atmosphere through the reduced pressure ejectors posing a potentially lethal occupational hazard for desalination workers; and (3) a third fraction of the agent will be capable of evaporating in the early stages of MFD and co-distill, with the distillate posing a threat to consumers.

Lindesten and Schmitt reported the results of an investigation conducted by the USA Army in the fall of 1962 (at the Chemical Corps Test Area, Graces Quarter, Maryland) to evaluate field-distillation units for the decontamination of water spiked with CWAs. The data generated by this investigation as given in table 1, revealed that the distillation was adequate to eliminate blistering HD and HN-3 agents from the treated water by nearly 100 percent.[9]

In Reverse Osmosis

Many factors determine the efficiency of RO membranes in rejecting blistering CWAs. Foremost are the size and shape of the molecule, the electrical charge, and the basic compatibility with the RO membrane. However, it is possible for certain organic molecules to pass through the membrane more easily and rap-

Table 1: CWAs decontamination by distillation.[10]

CWA	volatility (mg/m^3) at 25°C	(mg/1) of CWA in feedwater	(mg/1) of CWA in distillate	percent removal achieved	percent removal required	MPC in (mg/1)
HD	610	3.4	0.0	100	41.2	2.0
HN-3	121	23.6	trace	?	91.5	2.0

idly than water itself. In this circumstance, the product water is actually richer in solute than the feed water, a phenomenon referred to as "permeate enrichment."

Even though desalination (either via distillation or RO treatment) is theoretically very efficient in removing blistering CWAs at different degrees, residues of these agents are likely to infiltrate and breakthrough into the treated product posing a serious hazard to consumers. Additional measures should be taken to further reduce residual toxicants in desalinated water to the acceptable MPC levels prior to public distribution.

GENERAL FATE OF CWAs IN THE MARINE ENVIRONMENT

The fate of blistering CWAs in water is largely determined by their aqueous solubility. Based on the solubility, one can easily predict if droplets of the released agent into a body of water will go into solution or alternatively sink to the bottom, laying in globs in depressions and crevices. Although surface tension conceivably could hold some of the agent on the water surface, agitation and wave action should enable the redistribution of the contaminating agents according to their solubilities.

According to Trapp, blistering agents HD is soluble to 0.8 g/l at 20°C and HN-3 is soluble to 0.16 g/l at 0.5°C. The solubility of CWAs is fairly temperature dependent, increasing at elevated temperatures. The hydrolysis data obtained under laboratory conditions in homogeneous phase are an inadequate guide to what may happen under environmental conditions. Due to their low solubility, the rate of degradation of HD will depend mainly on the contact surface between the agent and the water.[11]

Hydrolysis

For that part of the agent-contamination which does indeed dissolve, the available published laboratory data on hydrolysis in homogeneous mixtures can be used to estimate natural degradation in water. But with respect to less

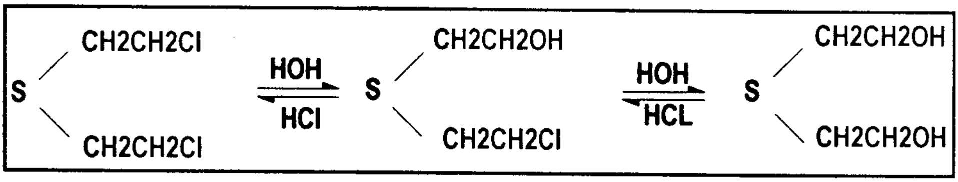

Figure 1a: Hydrolysis of HD in water.

soluble or insoluble agents, the situation is much more complicated. The rate of degradation may be determined either by the rate of hydrolysis where this is relatively slow, or by transport phenomena and the available contact surface between the two phases, or by both together.

Hydrolysis of HD

Sulfur mustard HD has a higher specific gravity than water. Because of its surface activity, HD reduces the surface tension of water and a small fraction of it spreads in a thin film on the water surface. In water, HD will hydrolyze by substituting its chlorine atoms with hydroxyl groups from the aqueous

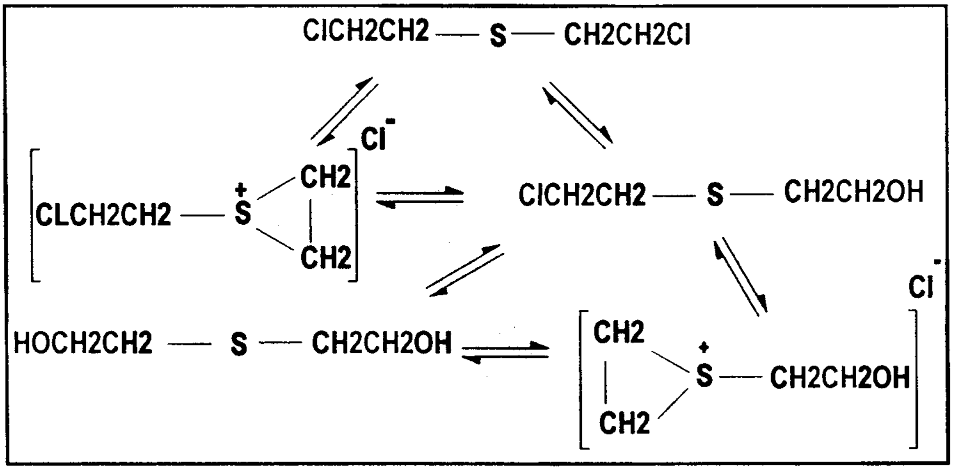

Figure 1b: Intermediates formation during HD hydrolysis.

medium. The reaction is reversible in its first stage by excess hydrochloric acid. In general, it runs according to the reaction given in figure 1a with the formation of the non-poisonous [bis-(2-hydroxyethyl)-thioether]. On the basis of the capacity of the thioethers to form tertiary sulfonium compounds, it was later found that during the hydrolysis, intermediate cyclic sulfonium ions are formed, so that the reaction mechanism can be assumed as depicted in figure 1b.[12] The reactions are classical example of "anchimeric assistance," i.e., dramatically accelerated by neighboring group (sulfur atom) participation. The

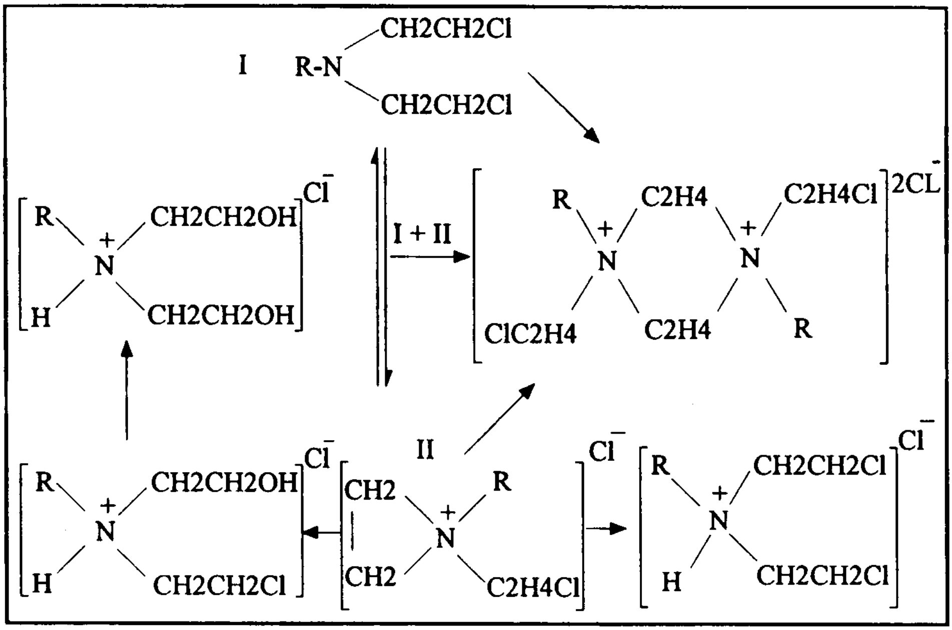

Figure 1c: Hydrolysis of N mustard in water.

reaction kinetics are essentially first order due to the fact that the rate controlling step is the formation of the cyclic sulfonium ion. The reaction has a half-life of approximately 4–5 minutes which, although unsatisfactory for emergency decontamination, is sufficiently fast when time is not a prime factor. The problem with mustard hydrolysis however, is the limited rate of solubility of the material. Sides *et al.* has reported a solubility rate of 1.2 x 10^{-5} g cm^2 min^{-1} for dissolution of mustard in water.[13]

The possibility of formation of tertiary sulfonium compounds is linked to the dimerization of the non-hydrolyzed [bis-(2-chloroethyl)-thioether] with its hydrolysis products obtained according to the equation in figure 1a and/or to the dimerization between the hydrolysis products and further -merization phenomena. These products hydrolyze to the final product of hydrolysis, [bis-(2-hydroxyethyl)-thioether]. The time courses for HD hydrolysis in aqueous systems have been reported with wide variations. According to Franke, 110 minutes were required for 99 percent hydrolysis of an HD-saturated solution (0.08 percent) at 20°C.[14] An originally saturated-mustard solution still contains 15 percent of the non-hydrolyzed thioether (120 mg/l) after 2.0 hours at 15°C. Solutions of this concentration are said not to have any skin-damaging effects. The data compiled by Franke are listed in table 2. Further data on HD hydrolysis as reported by the US Department of the Army, indicates that in distilled water at 25°C the half-life of HD is 8.5 minutes.[15] In seawater at the same temperature, the half-life was estimated at 60 minutes. As table 2 indicates, the rate of hydrolysis is accelerated with rising temperature. Water which contains a small amount of HD (around 1 percent) can be decontaminated by boiling it for 15 minutes.

The hydrolysis of N mustards also involves the formation of an onium ion, as illustrated in figure 1c.

Photodegradation

Photodegradation concerns itself to the small fraction of blistering CWA into the uppermost water masses. Although not significant, photodegradation can ultimately affect the fate of CWAs in the aquatic environment to a limited extent. Harris has estimated that photophysical deactivation to the ground state of the CWAs molecules with no net chemical degradation, generally account for more than 95 percent of the light energy absorbed.[16] Thus, it can be concluded that the potential for photolysis of blistering CWAs after dissemination would be insignificant.

Biodegradation

Almost all the reactions involved in microbial degradation can be classified as reduction, oxidation, hydrolysis, or conjugation.[17] Most of the research in this field were found to be descriptive, focusing on identification of the organisms responsible for the degradation of specific substances (Morrill *et al.*, 1985; Alexander, 1977; and Scov, 1982).[18,19,20] Since blistering mustard agents are cell poisons of low specificity, it might be expected that most water microorganisms will not survive high water concentrations of mustard. This could mean that microbial degradation may only be a minor mechanism of mustard water biodegradation. According to Trapp (1985), beexoenzymes of bacteria may exist which are capable to transform mustard via oxidizing pathways into less toxic metabolites. Therefore, mustard biodegradation by water microorganisms should be rather slow compared to degradation via hydrolysis.

Table 2: The hydrolysis of saturated aqueous solutions of HD after 2 hours at various temperatures.[24]

Temperature in °C	percent Hydrolyzed HD	Non-hydrolyzed HD in mg/l
0.6	41	197[a]
10.0	78	154[a]
15.0	85	120[a]
20.5	–	10

a. Extrapolations.

FATE OF CWAs IN THE KUWAIT MARINE ENVIRONMENT

The water quality and prevailing marine environmental conditions have significant impacts on the fates of different CWAs.[22,23,24,25,26,27] It has been generally noticed (from the limited and scattered open literature) that the parameters of reported effect were found to be as follows:

- Temperature
- pH
- Salinity
- Divalent metals (copper, calcium, and magnesium)
- Current and turbulence within the area of spilling

Because of the low solubility of blistering CWAs in water, water usually remains contaminated for a long period of time, depending on the amount of the agent, since newly released CWA is constantly diffusing in small amounts into the water in the place of that which has been hydrolyzed. Experience shows that a large volume of the CWA which is in or under the water continues to stay effective for years if the water is still or moving very slowly. Since most blistering CWAs are practically water insoluble, the hydrolysis can take place only immediately at the phase boundary.[28,29] For rapid hydrolysis, a certain turbulence is necessary. If this is lacking, especially in the case of industrial type of s-mustard due to impurities and admixtures contained in them, the formation of a third phase comes about, which in s-mustard is slightly soluble and which protects the CWA against further hydrolysis and preserves it under water. In sum, for the complete hydrolysis of blistering CWAs, a great excess of water and either turbulence or heat are necessary; it is still better if all three factors are in play.

Effect of Ambient Temperature

In Kuwait, the seawater temperature is controlled by the meteorological conditions. It usually follows the variation of air temperature with a given time delay. According to Literathy *et al.* 1985, the usual surface to bottom temperature difference is between 0.5 and 1.5°C. However, in the deeper offshore areas, significant temperature stratification could be observed in summer. Generally, the overall minimum and maximum temperature readings range from 15 to 34°C in winter and summer respectively.

In such a relatively warm-water-temperature, the rate of hydrolysis of HD should be accelerated significantly. Extrapolation of the data provided by Franke indicated that 100 percent of a saturated solution of HD in fresh water will be hydrolyzed in about 2 hours at 20°C.[30] However, in seawater at 25°C, the half-life of a saturated solution of HD will extend for one hour. In Kuwait, at the average minimum winter recorded temperature, it is expected that HD toxicity will last much longer than in summer. In summer, where water temperature can reach 35°C, it is expected that the rate of hydrolysis will be much faster. The most likely half-life for HD saturated seawater will be a few hours, while in summer, the most likely half-life should not be more than one hour. This prediction should be treated very carefully, since it is based on incomplete and unverified data. Additional factors are involved in the hydrolysis process, and our prediction is restricted to water contaminated with HD at or below saturation only. At levels higher than the 100 percent saturation, other factors will be controlling the hydrolysis process in addition to temperature.

Effect of pH

The pH value for the coastal waters of Kuwait ranges between 8.2 and 8.3 standard units during the whole year. The maximum variable range is +/- 0.2 units. These values indicate a well-balanced aquatic system.[31]

In water, HD will hydrolyze by substituting its chlorine atoms with hydroxyl groups from the aqueous medium.[32] Based on this fact, it was possible to assume that hydrolysis of HD is promoted in basic media, while it is hindered and retarded in acidic media. From the regularly reported pH values in the near shores of Kuwait, it is possible to predict an accelerated rate of HD degradation. The lack of data in open literature obstructed attempts to verify this prediction.

Effect of Salinity

The Arabian Gulf is a nearly landlocked shallow sea with relatively high rate of evaporation and very limited fresh water input. These factors have contributed to comparatively higher salinity. The salinity values observed range from 3.7 percent to 4.1 percent depending on the season and sampling locations.[33]

In case of seawater contamination by HD agent at levels below saturation, the data reported by the Department of the US Army suggests that the rate of its hydrolysis will be much slower compared to fresh water.[34] Based on such data, it was projected that the half-life of HD contamination in the coastal waters of Kuwait below the levels of saturation at 20°C should be not less than one hour. In general, data concerning the fate of HD in water has to be treated with extra care. They seem to suggest a rather fast degradation at least in low salt water (though the one hour half-life in seawater also seems to guarantee rapid degradation). This however, is commonly not the case, simply because HD hydrolysis in water is a surface controlled process.

Effect of Divalent Metal Content

Studies conducted by Epstein illustrated the catalytic effect of metal ions on the rate of hydrolysis of CWAs.[35] By adding 1.0 mg/l copper to water contaminated with the CWA Sarin, the half-life was reduced from 175 to 2 hours only. Relatively small concentrations of metal ions can markedly accelerate the rate of CWAs decompensation in water. The ions present in seawater that might be expected to contribute to hydrolysis rate are metal-hydroxy ions and hydroxide ions. However, it is expected that the primary ions present in seawater that could affect the rate of hydrolysis are calcium and magnesium.

The distribution of copper in the coastal waters of Kuwait ranged from 0.7 to 13.8 Ug/l.[36] The levels of calcium and magnesium ranged from 510 to 650 mg/l and from 1400 to 1800 mg/l respectively).[37,38] The direct impact of these ions is not clear due to the scarcity of published information. However, the general consensus is that the presence of these metal ions in seawater will dramatically accelerate the hydrolysis process.

Effect of Currents

Hydrolysis of over-saturated HD solutions is mostly transport/surface controlled. According to Trapp (1985), leaking containers of HD that had been sunk in the Baltic Sea after World War II are still being encountered in which the bulk of the agent remains as dangerous as it was when dumped—being protected against seawater attack by its solid state, its very low solubility, side products of hydrolysis and dimerization products forming a protective phase when turbulence is lacking, and by the container itself. Similar effects had led to accidents with CWAs in certain coastal zones of Japan, where Japanese CWAs were dumped after World War II.[39] The hydrolysis rate determining factor is not necessarily the seawater characteristics, but simply the turbulence and the temperature affecting the solubility. For these reasons it seems important to study the currents and turbulence patterns observed in Kuwait's coastal waters. The data available are basically for Kuwait Bay.[40]

The territorial waters of Kuwait are characterized by active tidal cycles.[41] From the general hydrodynamic features, it is expected that in case of massive contamination of seawater with low solubility HD, this agent will have the necessary turbulence needed for the hydrolysis process to proceed continuously till the exhaustion of the agent from the aquatic system.

In case of Kuwait seawater contamination by HD at levels below saturation (such as in case of drifting of mustard gas plumes from land based military operations), the described surface-controlled phenomenon will have very limited impact. However, in case of enormous releases of these agents (such as in case of massive disposal or sinking of loaded cargo ships near the shorelines), the hydrodynamics of the coastal waters will bring up the deposited CWA to the water column while hydrolysis is taking place at its own pace. This process can lead to the following:

- Extended toxicity of the agents by rendering them available in the soluble form, causing severe damage to the marine ecology and possibly to humans coming in contact.
- The non hydrolyzed fraction of the toxic agent can reach the power/desalination plants intakes.
- Hydrolysis will be proceeding without interruption until the exhaustion of the agent.

It is important to note that in case of a land-based mustard gas assault, it is very unlikely that the drifting levels of the released agent will exceed its solubility in seawater. However, in the event of massive marine releases near to the shorelines, the phenomenon of extended toxicity should be taken seriously by government authorities.

IMPACT OF DESALINATION PROCESSES ON THE FATE OF BLISTERING CWAs

During desalination, seawater is subjected to different treatment processes that can alter the immediate fate of the CWAs of concern. Among the most important processes that can affect the fate of CWAs in thermal desalination are chlorination and exposure of these agents to heat. In case of RO desalination, the feed water is subjected to extensive pre-treatment which includes chlorination, coagulation, sedimentation, filtration and dechlorination, before pumping to RO membranes. These pretreatment processes can be instrumental in the removal and/or detoxification of the blistering CWAs.

In Thermal Desalination

Thermally desalinated water is chlorinated twice. Once at the seawater intake to control biofouling, and a second time at the point where potable water leaves the plant for disinfection purpose. The regular daily doses at the intakes ranges from 2 to 4 Part Per Million

PPM) of chlorine injected unceasingly. Additional shock doses are added systematically every 8 hours for 20 minutes durations at 8 to 10 ppm concentrations.

Effect of Chlorination on HD Agent

The reaction of HD with chlorine and sometimes other chlorinating agents such as chloramine, causes the formation of various chlorinated thioethers and slightly toxic sulfoxide, which is extremely stable to hydrolysis, and then to sulfone which is slightly toxic but vesicant.[42] Depending on the number of chlorine atoms and their position in the molecule, these chlorination products have only slight physiological effect or none.[43] The reaction pathway of HD with chlorine is illustrated in figure 2.

According to Lindesten and Des Roches, saturated solutions of HD can be decontaminated with 350 ppm chlorine at 20°C. The water can be drunk without misgivings after filtration through activated charcoal.[44]

Effect of Heat on Blistering CWAs in Thermal Desalination

Steam generated for electric power production is diverted to MFD for water distillation. In the event of feed water contamination with blistering CWAs at the intakes, the agents will be subject to various cycles of heat, pressure and vacuum. The impact of heat on the fate of the CWAs of interest will be projected based on available data from open literature. The thermal decomposition (temperature at which a substance breaks down into other substances) of CWAs ranges from 149°C to about 170°C for HD.[45] In this context, thermal decomposition is not the main concern since the operating temperature in the desalination industry is lower than 120°C. However, The rate of hydrolysis of organic chemicals generally increases with the temperature. The relationship between the hydrolytic constant (k) and temperature is frequently expressed by the Arhenius equation as follows:[46]

$$k = s e^{-H_a/RT}$$

Where s = frequency factor
H_a = heat of activation (kcal/mole)
R = gas constant (1.987 cal/deg. mole)
T = temperature (°K)

In theory, the temperature dependence of k is more complex than the equation would suggest because s and H_a are themselves temperature dependent. For temperature ranging from 0°C to 50°C, the expected impact on the hydrolytic rate constant were projected by Harris as follows:[47]

- A 1°C change in temperature will cause a 10 percent change in k.
- A 10°C change in temperature will cause a factor of 2.5 change in k.
- A 25°C change in temperature will cause a factor of 10 change in k.

Because of the high sensitivity of k to changes in water temperature, a variation of 25°C would cause a 10 fold (1000 percent) increase in the hydrolysis rate of the CWAs.

The impact of heat on the rate of blistering agent HD hydrolysis is best illustrated in table 2. It has been noticed that within reaction duration of 2 hours, the fraction of hydrolyzed HD increased from 41 percent to 85 percent by raising the temperature from 0.6°C to 20.5°C. At the regular operating temperature in the power-DPs (90°C-120°C), it is projected that the rate of hydrolysis should be orders of magnitude faster than the reported values.

Effect of Pretreatment on the Fate of CWAs in RO

The common practice in RO desalination of seawater is to prechlorinate continuously at 2 to 4 ppm and occasionally apply shock doses for biofouling control. The feed water is then dosed with coagulant and coagulant aids for the

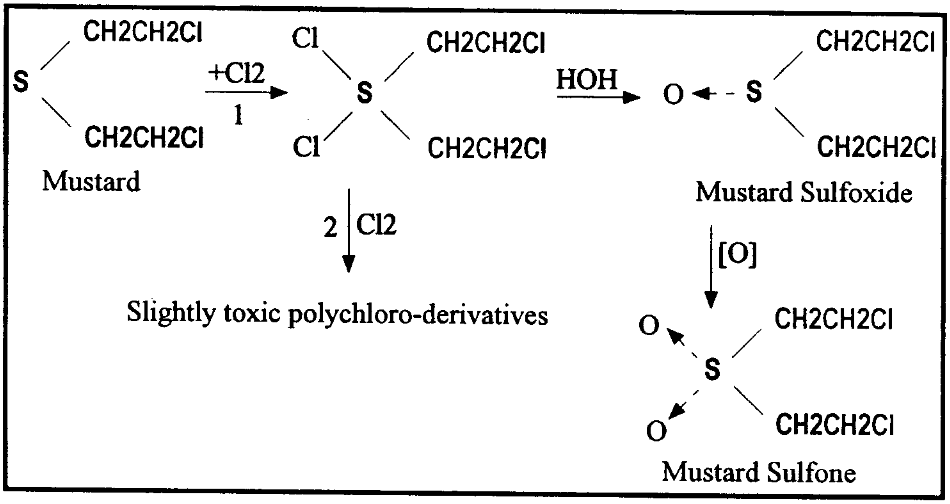

Figure 2: Major reactions of chlorine with HD (Franke 1977).

removal of dispersed suspended and colloidal particles. Following agglomeration, flocculation (i.e., formation of heavy aggregates and clusters of suspended particles), and settling of particles, the supernatant (i.e., top layer of clarified water) is filtered through a dual media, dechlorinated and then finally conveyed to RO units for desalination.

Data related to the impact of pretreatment unit processes and operation on the fate of CWAs are not available in the unclassified literature. However, based on theoretical considerations, it is expected that pretreatment is very likely to reduce the toxicity of CWAs for one or more of the following reasons:

- Prechlorination of the feed waters as applied in the thermal desalination processes will result into the degradation and then decontamination of the CWAs as discussed earlier.
- Coagulants and coagulant aids will form flocs (i.e., heavy aggregates of suspended particles tied to the added coagulant) of large surface characteristics. This phenomena will undoubtedly reduce the level of CWAs in the feed waters through physical processes such as adsorption, absorption, and co-precipitation on the surface of the formed flocs (known as sweeping flocs).
- The detention time needed for the fulfillment of the pretreatment of the feed waters will provide contaminating CWAs the opportunity to hydrolyze.

MEASURES TO MANAGE AND CONTROL BLISTERING CWAs IN DESALINATION PLANTS

Measures for the control and decontamination should be established since it is essential that safe potable water is provided to the public. In the event of an attack, the selected measures will heavily depend on the nature and the amount of the CWA released.

The relatively high temperature and pH characterizing the seawater in Kuwait, especially, when coupled with long traveling time (time needed for the blistering agents to reach DP intakes), will collectively eliminate any opportunity for the blistering agent to reach the intakes before being totally hydrolyzed to harmless compounds. Furthermore, when seawater is processed for power generation and potable water production, it will be subject to chlorination and thermal exposure leading to further degradation of the agents. It is safe then to presume that whenever seawater is contaminated with moderate levels of blistering agents (around 1 percent), at a distance far enough for hydrolysis and dilution to take place, this level will most probably pose no threat to the produced drinking water quality.

Hydrolysis was recommended by Lindesten and Schmitt for the decontamination of water containing blistering CWAs such as HD, HN-1, HN-2, and HN-3.[48] They also recommended the removal of the hydrolysis products using 600 ppm of activated carbon.

A series of recommended management and control measures aimed at minimizing the hazard of exposure to CWAs via desalinated seawater are given in the flow diagram illustrated in figure 3. These measures are not guaranteed to eliminate the risk but will certainly minimize it. The recommended measures are based on the scientific considerations discussed earlier, verified reported testings, operating desalination processes, dominating marine environmental conditions in Kuwait, and technical feasibility and reliability.

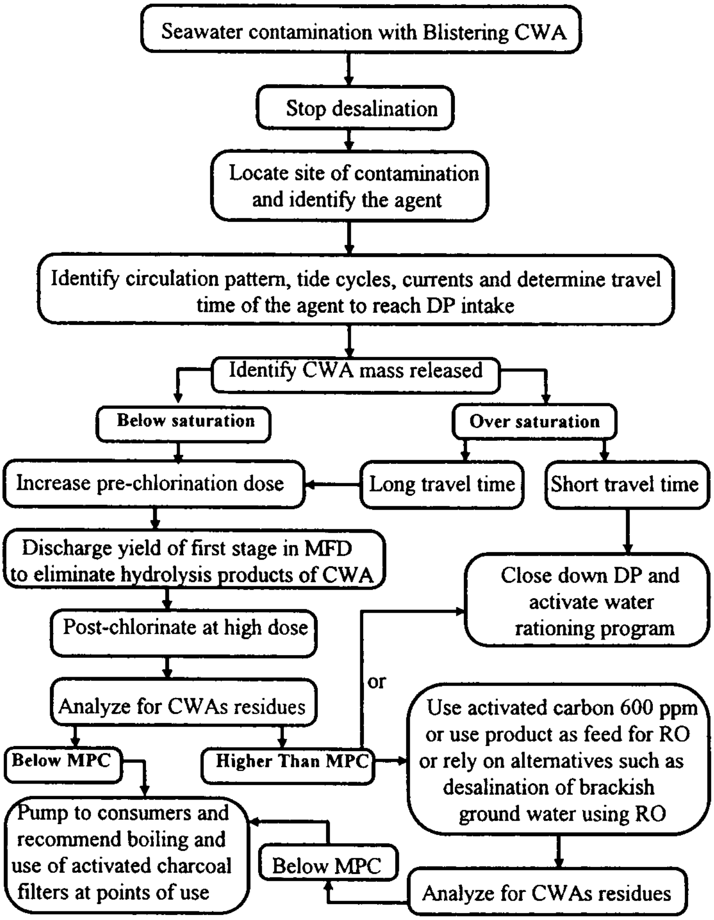

Figure 3: Flow diagram of recommended measures for the management and control of CWA contamination at the intake of a desalination plant.

In the event of blistering CWA contamination in Kuwait seawater, the following protection measures can be adopted instantly:

- Stop desalinated drinking water production for one day during summer and two days during winter. This procedure will allow the CWAs in solution (i.e., below saturation) to hydrolyze and dilute before being processed for distillation.
- Locate the site of the contamination and identify the nature of the agent with the help of the local defense authorities.

- From the local hydrodynamic circulation patterns and tidal cycles calculate the travel time needed for the agent to reach the desalination plant intakes by using mathematical models developed locally to predict the transport of water contaminants of similar nature.
- Identify the mass of the discharged agent to estimate the rate of chemical releases through dissolution. The span of the episode can then be figured based on the agitating hydro-currents, sea conditions, solubility of the agent and temperature.
- whenever desalination is resumed, pre-chlorination doses should at least be doubled to accelerate the catalysis and/or oxidation of any potentially remaining agent;
- Discharge the yield of the first stage in MFD to minimize and possibly eliminate CWAs hydrolysis products from reaching finished waters.
- Post-chlorinate at higher doses and extend the holding time in finished water reservoirs prior to distribution to achieve complete degradation of any remaining residues.
- Administer high doses of activated carbon to catalyze, and adsorb persisting agents and their hydrolysis products.
- Analyze for traces of blistering CWAs before distribution.
- In case of contamination with blistering agents at levels below saturation, resume seawater desalination after one day of cessation without additional treatment measures.
- In the case of heavy contamination (i.e., over-saturation), resume production after two days of cessation and use thermally desalinated water as feed water for RO units. This hybridization process will eliminate any potential existence of residual CWAs, and will prolong the life span of RO membrane while increasing its capacity.

It should be noted that stocks of activated carbon, soda ash, active sodium hypochlorite and/or dechlorinating agent should be available for potential use in case of emergency.

Analytical testing procedures and protocols should be made available to test drinking water for CWAs prior to distribution.

RESEARCH NEEDS

Because of the lack of information on the characteristic of the blistering CWAs of interest, their likely method of dissemination or release, and the complex nature of the Arabian Gulf marine environment, it would be extremely difficult to quantify any specific aspect of interaction between the aquatic environment and a given CWA. The impact of seawater desalination processes on the fate and removal efficiency of blistering CWAs from feed water was never addressed or reported in the open literature. The scarcity of information in this domain was mainly attributed to the following reasons:

- Most of the information inquired by military research institutions have not been disclosed and are classified as confidential.
- Contamination of drinking water generated via seawater desalination with CWAs is regarded by the scientific community as a distinctive regional problem confined mostly to the Arabian Gulf region and has very limited international applications.
- Oceans and water bodies in general are not common targets for CWAs attacks.
- In case of contamination, human body contacts with water (i.e., exposure) can be controlled as compared to air or soil contamination. This fact reduced the interest in defining the exact fate and pathways of these agents in aquatic environments.
- The recent proliferation of CWAs as weapons of mass destruction in the Arabian Gulf region and their potential impact on its vital desalination industry is relatively new and were never carefully thought about.
- In most of the published information, priority was always given to research strictly dealing with decontamination techniques of drinking water from CWAs. These efforts were mainly aimed at granting potable waters for armies in combat.

Several major gaps existed in the knowledge needed to accurately determine the fate of blistering CWAs and their impact on desalinated drinking water quality in Kuwait. Among these gaps the following can be listed:

- The regional marine environmental factors known to affect the natural degradation processes of CWAs in Kuwait are very unique and peculiar. Research should focus on these factors such as seawater chemical composition, pH, temperature, hydrodynamic regime, falling light intensities and durations, and microbial populations.

- Comprehensive understanding of interaction between different simultaneous natural degradation processes of CWAs in aquatic systems as a whole is rather poor today, even in similar situation where detailed knowledge of most of the contributory processes is available. It is inevitable to investigate the mutual impact of concurrent degradation processes on the rate of detoxification of the CWAs of interest.
- Even though information inquired by military research institutions around the world have not been disclosed, available knowledge concerning modification in the properties of the CWAs, their means of delivery and deployment, and toxicity, decontamination and developments in detection techniques should be searched and compiled in data bases.
- Evoke all the factors and processes involved in the behavior of CWAs in seawater to construct mathematical predictive models capable of projecting the persistency of certain agents in Kuwait's seawater under various environmental conditions.
- Determine the rate of natural detoxification under existing environmental conditions and use the yielded half-life human toxicity data to calculate time spans needed for the reduction of hazardous to innocuous concentrations.
- Development of a research facility to conduct research on the impact of different desalination unit processes and operation on the removal of CWAs from feed seawater. Emphasis should be given to impact of chlorination, heat, and detention time on the toxicity and fate of the CWAs. Toxicity of degradation products in finished water should not be discounted.
- Development of contingency plans for management of CWAs emergencies and study methods of artificial decontamination, containment, and procedures for warning and protection of civilians.
- Develop or adopt analytical methodologies and bio-indicator techniques for the early detection of CWAs residues in desalinated drinking water.

CONCLUSIONS

Contamination of seawater with blistering CWAs can be naturally alleviated by degradation mainly through hydrolysis. Hydrolysis is a relatively fast pathway as compared to other processes such as biodegradation and photooxidation. From the review of the open literature and based on the marine environmental conditions in Kuwait, the following projections can be made:

- Hydrolysis will affect the soluble fraction of blistering CWAs only.
- The rate of degradation of insoluble agent is determined by the transport phenomena and the available contact surface between the two phases (water/CWA).
- Higher temperature will promote degradation of blistering CWAs by increasing their solubilities and by accelerating their hydrolysis reactions.
- Higher pH, and divalent metal content (Cu, Ca, and Mg) in the ARABIAN GULF will promote the hydrolysis of CWAs. However, higher salinity will reduce the rate of HD hydrolysis.

In general, all the environmental factors involved in the aquatic degradation of CWAs in Kuwait marine environment except for the high salinity in case of HD, are in favor for a fast degradation process. In case of massive releases of CWAs near the Kuwaiti shorelines, turbulence resulting from tidal cycles and high temperature will affect the dissolution process and extend the toxicity of the insoluble agent. However, this phenomenon will lead to a faster elimination of the toxic substance from the aquatic environment. The time needed for the transport of the soluble fraction of the agent from the point of release to the intakes of desalination plants should be calculated to estimate the likely residual levels of toxic non-hydrolyzed fractions of the agent.

Post- and pre-chlorination during the course of seawater desalination will catalyze and significantly accelerate the hydrolysis processes of the CWAs. The heat exerted on CWAs during the power generation-desalination processes is not expected to thermally decompose them. However, the steam heat will augment the agent's rate of hydrolysis with subsequent acceleration in their rate of detoxification.

Conventional pretreatment of feed seawater for RO desalination is theoretically capable of reducing the concentration of CWAs by coprecipitation and adsorption on flocs formed during coagulation. Prechlorination and prolonged detention time in pretreatment units will simultaneously promote hydrolysis reactions. However, in case CWAs succeed to reach RO membranes, they can break through them into the permeate at levels higher than the accepted tolerance posing a potential life threat to the public.

Suggested control measures included boosting of pre- and post-chlorination doses, discarding the yield collected from the first stage in MFD, applying high doses of activated carbon, extending detention time, and utilizing water treatment devices at point of use and/or boiling the water by consumers.

REFERENCES

1. New Scientist, “Gas victims arrive in London”, Anonymous, (March 28, 1985), p. 5.

2. Norman, C., “CIA details chemical weapons spread”, Science Vol. 243, (1989), p. 888.

3. Zanders, J.P., “Chemical weapons proliferation in the Gulf region and the strategic balance after Operation Desert Storm”, The International Conference on the Effects of Iraqi Aggression on the State of Kuwait, Kuwait, (April 2–6, 1994).

4. Norman, *op. cit.*, p. 888.

5. Zanders, *op. cit.*, (April 2–6, 1994).

6. Lindesten, D.C. & Schmitt, R.P., “Decontamination of water containing chemical warfare agents,” National Technical Information Service, Springfield, Virginia, Report No. AD-A 012 630, (1975), p. 103.

7. ibid.

8. Kuwait Ministry of Electricity and Water, Statistical Year Book, Al-Kabas Press, Kuwait, (1989).

9. Lindesten, *op. cit.*, p. 103.

10. Modified from Lindesten and Schmitt, (1977), and the U.S. Department of the Army, (1975).

11. Trapp, R., “The detoxification and natural degradation of chemical warfare agents,” Stockholm International Peace Research Institute (SIPRI), Taylor and Francis, London, (1985), pp. 12-8.

12. Franke, S., “Lehrbuch der Militaerchemie,” 2 vols. Militaerverlag GDR, Berlin, 512 + 615, (1977).

13. Sides, G.D., E.B. Dismukes and R.B. Spafford, “Evaluation of Decontamination Formulations,” final draft report, Southern Research Institute, Report on contract DAAK11-77-C-0081, Alexandria, Virginia, (1980).

14. Franke, *op. cit.*, (1977).

15. USA, Department of the Army, “Military Chemistry and Chemical Compounds,” US Department of the Army, Headquarters, Washington, Field Manual No. 3-9, AFR 355-7, (1975).

16. Harris, C.R., “Factors Influencing the Effectiveness of Soil Insecticides,” Ann. Rev. Entomol, 17, (1982), pp. 177-198.

17. Morrill, L.G., L.W. Reed, and K.K. Chinn, “Toxic Chemicals in the Soil Environment,” Technical Analysis and Information Office, US Army Dugway Proving Ground, Dugway, Utah, 85-8:20:075, (1985).

18. ibid.

19. Alexander, M., “Introduction of Soil Microbiology,” 2nd. Ed., John Wiley & Sons, New York, (1977).

20. Scov, K.M., “Rate of Biodegradation,” In “Handbook of Chemical Property Estimation Methods,” Layman W.J., W.F. Reedl and D.H. Rosenblatt, Eds., McGraw-Hill Book Co., New York, (1982).

21. Franke, S., *op. cit.*, (1977).

22. Larsson, L., "The Alkaline Hydrolysis of Isopropoxy-Methylphosphorylfluoride (Sarin) and Some Analogues," Acta Chemica Scandinavica, Copenhagen, 11, (1957), pp. 1131-42.

23. Franke, S., *op. cit.*, (1977).

24. Lindesten, *op. cit.*, p. 103.

25. Epstein, J., "Properties of Sarin in Water, Water Technology and Quality," *Journal of the American Water Work Association*, 66, (1974), pp. 31-37.

26. Lindesten, D.C. & Des Roches, P.R., "Decontamination of Water Containing Chemical and Radiological Warfare Agents by Reverse Osmosis," National Technical Information Service, Springfield, Virginia, Report No. AD-A 046 203, (1977), p. 64.

27. USA, Department of the Army, *op. cit.*

28. Kurata, H., "Lessons Learned from the Destruction of the Chemical Weapons of the Japanese Imperial Forces," In Stockholm International Peace Research Institute (SIPRI), *Chemical Weapons: Destruction and Conversion*, Taylor & Francis, London, (1980), p. 201.

29. Lundin. J., "Stockpiles of Chemical Weapons and Their Destruction," In Stockholm International Peace Research Institute (SIPRI), *SIPRI Yearbook of World Armaments and Disarmament 1979*, Taylor & Francis, London, (1979), p. 698, pp. 470-89.

30. Franke, S., *op. cit.*, (1977).

31. Literathy, P., M.A. Ali, L. Al-Harmi, J.W. Lee and A.S. Farmer, "Monitoring of Oceanographic Characteristics and Baseline Studies of Oil and Non-Oil Pollutants in the Territorial Waters of Kuwait," Kuwait Institute for Scientific Research (KISR) (EES-49), KISR Report No. KISR1662, (1985).

32. Franke, S., *op. cit.*, (1977).

33. Literathy, *op. cit.*, (1985).

34. USA, Department of the Army, *op. cit.*

35. Epstein, J., *op. cit.*, pp. 31-37.

36. Literathy, *op. cit.*, (1985).

37. ibid.

38. Samhan, O., W. Shublaq, T.G. Gopalakrishnan, and F. Ghobrial, "Study of the Coastal Zone of Kuwait for Aquaculture Purposes," Kuwait Institute for Scientific Research KISR (EES-73), KISR report No. 2053, (1986).

39. Kurata, *op. cit.*, p. 201.

40. Literathy, *op. cit.*, (1985).

41. ibid.

42. Niemann, C., "Miscellaneous Analytical Studies," In "Chemical Warfare Agents and Related Chemical Problems," Chapter 39, Summary Technical Report of Division 9, NDRC, (1946).

43. Franke, S., *op. cit.*, (1977).

44. Lindesten, *op. cit.*, p. 64.

45. USA, Department of the Army, *op. cit.*

46. Yaron, B., "Some Aspects of Surface Interactions of Clays with Organophosphorus Pesticides," Soil Sci. 125:210-216, (1978).

47. Harris, C.R. *op. cit.*, pp. 177-198.

48. Lindesten, *op. cit.*, p. 103.

49. Franke, S., "Manual of Military Chemistry," vol. 1, "Chemistry of Chemical Warfare Agents," NTIS AD 849 86, (1967).

50. Torrisi, S.P., "Operation of the Chemical Agent Munitions Disposal System (CAMDS) at Tooele Army Depot, Final Environmental Impact Statement," Army, Aberdeen Proving Ground, Report DRCPM-DRD-SP-77039, NTIS, AD A062668, (1977).