CHEMICAL HAZARDS IN SEAWATER DESALINATION BY THE MULTISTAGE-FLASH EVAPORATION TECHNIQUE

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Contents

Summary

Seawater desalination by the multi-stage flash (MSF) evaporation technique is a relatively clean industry, involving the use of a limited number of chemicals. The impact of these materials and/or their reaction products on human health in particular, and the environment in general is considered. Chlorination of seawater is carried out to discourage marine life inside the distillers. Either chlorine gas or electrogenerated hypochlorite is used. Chlorine in seawater liberates bromine and produces trihalomethanes. In ammonia-polluted waters chloramines are also formed. The largest impact of chlorine is present at the outfall where residual hypochlorite, hypobromite, chlor- and bromamines eradicate the lower members of sea-fauna and adversely affect the higher members. Over-chlorination of potable water triggers asthma and raises serum cholesterol and lipo-proteins. The same waters raise the risk of bladder cancer.

Scaling in distillers is inherent to seawater chemistry. Techniques for combating scale formation involve controlled acidification of the water or the addition of scale-retardants. Additives based on polyphosphate enhance algae growth. Organic polymers are foreign to the environment and might cause unforeseen pollution.

Excessive scaling inside distillers affects heat transfer and requires an acid wash. This involves huge quantities of acids and corrosion inhibitors. By the end of the wash process large quantities of acidified seawater are released at the outfall. Until these are fully neutralized dramatic changes in the habitat are liable to occur. A case in which the decomposition products of a corrosion inhibitor led to temporary blindness is mentioned.

Brines discharged at the outfall carry measurable quantities of heavy metal cations, have a higher salt content and are at higher temperatures than the surrounding seawater. All factors are suspected to be behind the deterioration of the mangroves around the plant's outfalls.

The case of air (oxygen) is cited to show how a life-sustaining element can lead to the production of an environment-polluting substance. This happens when air leaks inside the distiller and causes corrosion of copper-base condenser tubes at the vapor side.

Oil dispersants are mixtures of crude organic solvents used to dissipate oil slicks. They are environmentally unfriendly substances which should not be used at or near seawater intakes.

Potable water conditioning involves addition of calcium, bicarbonate and soda lye. Care must be experienced when handling the last material.

1. Introduction

Arid countries which lack natural sources of drinking water and have a coastline usually turn to seawater desalination to secure their daily demands. Desalination is carried out mainly by the multi-stage flash (MSF) evaporation technique. Seawater desalination is a relatively clean industry, involving a number of chemical processes which are employed to overcome operation difficulties or to improve unit performance. These processes have been described many times and are well documented (Shams El-Din and Makkawi 1998). Unfortunately, some of the chemicals used and/or their reaction products are either harmful to human beings or are potential pollutants of the environment. The adverse effect of these substances on human being and the environment is seldom considered. Information regarding the reaction between these chemicals and the various components of seawater is meager and scattered over a wide area of sources.

This chapter attempts to bring together a description of the processes and the hazardous effect of the chemicals involved. The review is presented in the general context that human beings are an integral part of the whole eco-system.

2. Seawater Chlorination

Chlorination of seawater is carried out at the seawater intake to discourage marine life (shells, barnacles, prawns, small fish etc.) from getting access inside the distillers. There is no standard procedure for chlorination. The amount of reagents added and the regime of treatment differ from one locality to the other and are established mostly by trial and error. They depend on factors such as biological activity, temperature, turbidity, eventual presence of ammonia, NH_3, and hydrogen sulphide, H_2S, pollutants etc. An example of a treatment procedure is to inject chlorine gas at the seawater intake to ensure a residual chlorine content of 0.4 ppm (mgl^{-1}). This is complemented by shock dosing at 1 ppm for 1 hr every week, to prevent build-up of resistance.

Chlorination is carried out using either gaseous chlorine from cylinders or *in-situ* electrogenerated sodium hypochlorite. At ambient temperatures chlorine is a greenish

yellow gas some three times heavier than air. It has a boiling point of -34.6°C and a vapour pressure of 5.72 bar at 21°C (WHO 1997). It is transported in special steel cylinders containing gas over liquid. At a constant temperature the gas pressure in the cylinder remains constant as long as there is appreciable amount of the liquid present. Cylinders should neither be heated nor placed in hot areas as the vapour pressure of the gas in the cylinder rises quickly with temperature. Chlorine is a very reactive material and combines or reacts with practically all elements. The gas is dangerous to inhale and the exposure limit is 1 ppm (mg kg^{-1}) and is readily detected by its irritating odour. At 30 ppm it promotes coughing and at 1000 ppm it is fatal after few deep breaths. Chlorine reacts with seawater to produce hydrochloric- and hypochlorous acids: $Cl_2 + H_2O = HCl + HClO$. Both acids are directly neutralized by seawater alkalinity. In light (ultra-violet rays) hypochlorite ion decomposes to chloride ion and nacent oxygen: $ClO^- = Cl^- + \frac{1}{2}O_2$. The disinfection effect of chlorine gas is attributed to hypochlorous ion. Electrogenerated chlorine solutions contain an abundance of hypochlorite (usually around 5000 ppm). In all respects the solution reacts as chlorine gas in water. It has, however, the advantage of being less corrosive and more confined. Spillages of hypochlorite solutions are also easier to handle than a leaking chlorine gas cylinder.

The largest impact of chlorine on the environment occurs at the plant's outfall. There, the spent brine, containing some 0.2-0.25 ppm of residual chlorine, is continuously discharged to the sea. As the hypochlorite ion is a powerful oxidant, it raises the redox potential of water. Enzymatic and biological processes in living organisms are prone to be affected. Microorganisms are sensitive to changes in redox potential and will exhibit zero- or minor tolerance; they will readily perish. Anchored or stationary organisms (shells or corals) will also meet with the same fate. Higher forms of marine life, capable of willed motion (e.g. fish, crabs, etc.) will migrate from the infected area. Others, with higher tolerance limits, will remain in the area, with or without mutagenic changes. However, methods for dechlorinating spent brine are known. These involve treatment with sulphur dioxide gas, SO_2, resulting in a byproduct of burning S-containing fuel (Helz et al. 1985), exposure in aerated ponds (Khordagui 1992) or adsorption on activated carbon (Chen and Gan 1981). A recent publication described the reaction with hydrogen peroxide, H_2O_2; $H_2O_2 + ClO^- = Cl^- + H_2O + O_2$ (Shams El Din and Mohammed 1998). This reaction is said to be fast, cheap and environmentally-friendly.

Confined seawater might contain appreciable quantities of ammonia, NH_3, and hydrogen sulphide, H_2S, resulting from the putrefaction and decay of living organisms. Chlorine reacts with NH_3-polluted water to produce mono-, di- and tri-chloramines (AWWA 1071). The chloramines posses biocidal properties which decrease in the succession mono- > di- > tri-substitution. The redox potential also varies in the same order. Both characteristics are weaker than with chlorine itself. On the other hand, chlorine oxidizes H_2S to elemental sulphur: $Cl_2 + H_2S = 2HCl + S$ thus reducing thus the dangers of H_2S-induced corrosion of the distiller's metals (Fontana and Greene 1978).

Chlorination affects seawater in two other ways which have adverse impact on human beings and the environment. The first involves bromine formation. Natural seawater contains some 65 ppm of bromide ion, Br^- (Hömig 1978). These react with chlorine to

produce elemental bromine according to $2Br^- + Cl_2 = Br_2 + 2Cl^-$ and the reaction is favoured by a standard free energy decrease of $\Delta G = -13.550$ kcal mol^{-1} (Latimer 1964). In view of the large concentration of Br$^-$ compared to Cl$_2$, it is unlikely that any free chlorine (ClO$^-$) will be found in water. What is commonly considered and measured as residual chlorine is in fact residual bromine. The reagent used for the determination of the former, viz., N-N-diethyl-p-phenylenediamine (DPD) (AWWA 1971) responds in much the same way to brominated water. Similar to chlorine, bromine, Br$_2$, reacts with water to produce hydrobromic and hydrobromous acids Br$_2$ + H$_2$O = HBr + HBrO. However, due to its limited solubility in water, elemental bromine collects and evolves as such with other non-condensible gases of the ejector (Oldfield and Todd 1987). On its way to the atmosphere, bromine gas can seriously attack the tubes of the ejector condenser (Lee et al. 1983). In presence of ammonia, bromine in water yields the corresponding bromamines. The biocidal activity of the bromamines is lower than that of the chloromines.

The second effect concerns trihalomethane formation. Chlorine and bromine in seawater react with naturally occurring or man-made organics to produce halogenated hydrocarbons, of which the trihalomethanes, CHX$_3$, are the most abundant. Under conditions of MSF distillation the formation of bromoform, CHBr$_3$, and mixed bromo-chloro halomethanes is favoured over that of chloroform, CHCl$_3$, by the large size of the bromine atom (Shams El Din et al. 1991). The conditions allowing halomethane formation from Arabian Gulf water were extensively studied (Shams El Din et al. 1991). Most of the halomethanes formed in the distiller are either expelled from the deaerator with the non-condensible gases or discharged with the spent brine. A small portion condenses, however, with the distillate (Shams El Din et al. 1991). Trihalomethanes are potential carcinogens and their concentration in drinking water should not exceed few ppb (microgram l^{-1}) (WHO 1997). The halomethanes are relatively stable compounds. As means of removing them from potable water, hydrolysis with alkali, followed by neutralization was recently investigated (Shams El Din et al. 1998). The compounds decompose to formate ion, HCOO$^-$, and carbon monoxide (Shams El Din et al. 1998).

Because seawater does not contain iodide ion in any measurable amounts, no iodohalomethanes have been detected in chlorinating seawater. These compounds form, however, under laboratory conditions when extra KI is added to the water (Shams El Din et al. 1992; 1998).

Chlorination of seawater can cause other damages. Chlorine gas leaking into the atmosphere of the desalination plant leads, under favorable conditions of wind direction and humidity, to atmospheric pitting corrosion of unprotected stainless steel and copper-nickel pipes (Shams El Din 1985). Long exposure under these conditions can lead to considerable material loss and to pollution of the environment.

Following the conditioning of the distillate (see later), potable water is chlorinated to the extent of 0.25 ppm, to ensure a residual content of 0.1 ppm at the consumer's end of the distribution line. Chlorination is carried out for disinfection purposes and should not exceed the specified limits (WHO 1997). Exposure to over-chlorinated water triggers asthma. Similarly, serum cholesterol and lipo-protein levels are high in communities

using over-chlorinated drinking waters. The same waters are said to raise the risk of bladder cancer (WHO 1997).

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