

THE INTERACTION OF CHLORINE AND SEAWATER, WITH SPECIAL REFERENCE TO THE FOUR LIQUID CHLORINE TANK CARS LOST IN BRITISH COLUMBIA COASTAL WATERS

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Summary

An examination is made of the various aspects of the interaction of chlorine with seawater in order to determine the form, fate and effects of chlorine when it leaks from the tank cars containing liquid chlorine which were lost while being transported on British Columbia coastal waters. Depending on temperature and pressure, four phases will be possible; gaseous chlorine, liquid chlorine, chlorine hydrate(s) and liquid water. At the expected water temperatures chlorine will remain as a liquid below 50 meters but gaseous chlorine could form above this depth. Mixing of liquid chlorine and seawater should cause only small temperature changes and gaseous explosion is not a threat at the water temperature involved. Density of the chlorine, chlorine hydrate and chlorinated seawater is higher than seawater and so should tend to sink. Some small scale release experiments show that the behaviour of liquid chlorine when injected into the water column conforms very well with the predictions based only on thermodynamics. Experiments show that seawater has a natural chlorine demand of about 1.5 mg/l in a half hour and twice that after two days. Although addition of chlorine to seawater will have a marked effect on pH, Eh, alkalinity and toxicity, dilution with about 2×10^8 m³ of seawater should result in the removal of chlorine through redox reactions, and a decrease of the alkalinity by only 2%.

Introduction

On February 19, 1975, four tank cars filled with liquid chlorine were lost from a barge being towed in the vicinity of Malaspina Strait in B.C. coastal waters. Although a series of searches was carried out [1], the exact location of the sunken cars has not yet been determined. Each tank car carried approximately 74 metric tons of liquid chlorine with a 15% void space padded to 6.9 bars with air.

Although there has been no evidence to date which might indicate that chlorine has leaked from the cars, it is only a matter of time before corrosion leads to failure of the tanks. How long this will take is an open question since it is not known exactly what condition the cars were in when they were lost or what sort of damage they might have received as a result of the accident.

The tank cars are constructed of five circumferential sections of 2 cm

(continued on p. 54)

STYLE 1/2 JQ 225			
ITEM	NAME OF PART	MATERIAL	PART NO
1	CAP	CAST IRON	59539
2	DIAPHRAGM - UPPER	3% ANTIMONY LEAD	32333
3	ADJUSTING BOLT	MONEL	39764
4	SPRING - COLORED RED	CARBON STEEL	32335 (STAMPED 630)
5	SPINDLE	STEEL	32335
31	BALL	CARBON STL. (HARDEN)	43927
6	LOCK NUT	MONEL	32315
7	DISC GUIDE	MALLEABLE IRON	32316
8	CASING	4" BRASS 1/4" FT PIPE	32317
9	SPRING WASHER - BOTTOM	STEEL - CARBON PLATED	32318
10	DISC BUSHING	STAIN STEEL	36324
11	DISC	MONEL	32319
12	GOTTER PIN	STAIN STEEL	28066
13	DISC INSERT	MONEL	32320
14	ADJUSTING RING	MALLEABLE IRON	32327
15	LOCK PIN	MONEL	39763
16	NOZZLE	"K" MONEL	39761
17	NOZZLE WASHER	3% ANTIMONY LEAD MILA 17472 (NAVY)	32322
18	BASE WASHER	3% ANTIMONY LEAD	32324
19	SAFETY MECHANISM WASHER	3% ANTIMONY LEAD MILA 17472 (NAVY)	32468
20	BASE	STEEL	32323
21	LOCKSCREW - CLIP SHAPED STD 1/4" 28 ALLEN HEAD SCREW 1/2" LONG	HARDENED STEEL	32326
27	SPRING WASHER - TOP	STEEL - CARBON PLATED	39762
BREAKING PIN & HOUSING DETAILS			
22	YOKE	STEEL	48886
23	BREAKING PIN - COLORED RED	ARMCO IRON ROD	48887
24	PLUNGER WITH COLUMNS	TYPE 304 STAIN ST.	69387
25	SPANNER NUT	MONEL	48889
26	CLIP	PIANO WIRE	48890
28	HOUSING	STEEL	48891
29	FOLLOWER	MONEL	48892
30	DIAPHRAGM - LOWER	3% ANTIMONY LEAD	48893
++ ALTERNATE			
23	BREAKING PIN - COLORED RED	SEE NOTE 6	84806

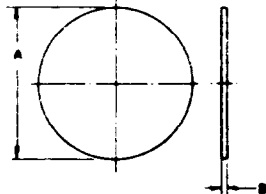
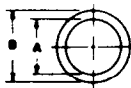
STYLE 1/2 JQ 375			
ITEM	NAME OF PART	MATERIAL	PART NO
1	CAP	CAST IRON	59539
2	DIAPHRAGM - UPPER	3% ANTIMONY LEAD	32333
3	ADJUSTING BOLT	MONEL	65083
4	SPRING - COLORED YELLOW	CARBON STEEL	32335 (STAMPED 630)
5	SPINDLE	STEEL	32335
31	BALL	CARBON STL. (HARDEN)	43927
6	LOCKNUT	MONEL	32315
7	DISC GUIDE	MALLEABLE IRON	32316
8	CASING	4" BRASS 1/4" FT PIPE	32317
9	SPRING WASHER - BOTTOM	STEEL - CARBON PLATED	32318
10	DISC BUSHING	STAIN STEEL	36324
11	DISC	MONEL	32319
12	GOTTER PIN	STAIN STEEL	28066
13	DISC INSERT	MONEL	32320
14	ADJUSTING RING	MALLEABLE IRON	32327
15	LOCKPIN	MONEL	39763
16	NOZZLE	"K" MONEL	39761
17	NOZZLE WASHER	3% ANTIMONY LEAD MILA 17472 (NAVY)	32322
18	BASE WASHER	3% ANTIMONY LEAD	32324
19	SAFETY MECHANISM WASHER	3% ANTIMONY LEAD MILA 17472 (NAVY)	32468
20	BASE	STEEL	32323
21	LOCKSCREW - CLIP SHAPED STD 1/4" 28 ALLEN HEAD SCREW 1/2" LONG	HARDENED STEEL	32326
27	SPRING WASHER - TOP	STEEL - CARBON PLATED	39762
BREAKING PIN & HOUSING DETAILS			
22	YOKE	STEEL	68195
23	BREAKING PIN - COLORED YELLOW	ARMCO IRON ROD	68196
24	PLUNGER WITH COLUMNS	TYPE 304 STAIN ST.	69387
25	SPANNER NUT	MONEL	48889
26	CLIP	PIANO WIRE	68197
28	HOUSING	STEEL	68198
29	FOLLOWER	MONEL	48892
30	DIAPHRAGM - LOWER	3% ANTIMONY LEAD	48893
++ ALTERNATE			
23	BREAKING PIN - COLORED YELLOW	SEE NOTE 6	84807

NOTES - GENERAL

1. THESE PARTS ARE PARKERIZED AND VARNISHED WITH GYPTOL, EXCEPT ON THREADS AND SLIDING SURFACES
2. UNDER A A R REGULATIONS - NO DEVIATIONS FROM NOTES A AND B ARE AUTHORIZED
3. THIS VALVE IS DESIGNED IN COOPERATION WITH THE CHLORINE INSTITUTE INC
4. THIS DWG SUPERCEDES DWGS D-13105 REV E & D-38615
5. SEE MAINTAINANCE INSTRUCTIONS FOR CHLORINE INSTITUTE STANDARD SAFETY VALVES, TYPE 1/2 JQ (C) PAMPHLET 39) FOR INSTRUCTIONS CONCERNING HANDLING, TESTING, INSTALLING, ETC
6. MAT. ASTM B-140 CU. ALLOY # 318

WASHERS			
ITEM	DIMENSIONS		
	A	B	C
17	1.31 32-3/32	2.11 52	1/16
18	4.3 16	4.7 16	1/16
19	2.32 64	1.5 64	1/16

DIAPHRAGMS		
ITEM	DIMENSIONS	
	A	B
2	4.32	3/16
30	1.52	3/16



NOTES - JQ 225

- A. BREAKING PIN MECHANISM IS DESIGNED FOR PIN (ITEM 23) TO BREAK AT 225 PSIG
- B. SET PRESSURE (SPRING SETTING) OF SAFETY VALVE ITSELF IS 20 PSIG FULL LIFT IS REALIZED AT 225 PSIG
- C. THIS VALVE IS FOR USE ON CHLORINE TANK CARS AND CARGO TANKS ONLY AT 225 PSI PRESSURE

NOTES - JQ 375

- A. BREAKING PIN MECHANISM IS DESIGNED FOR PIN (ITEM 23) TO BREAK AT 375 PSIG
- B. SET PRESSURE (SPRING SETTING) OF SAFETY VALVE ITSELF IS 360 PSIG FULL LIFT IS REALIZED AT 375 PSIG
- C. THIS VALVE IS FOR USE ON CHLORINE TANK CARS ONLY AT 375 PSI PRESSURE
- D. SPRING IS COATED WITH PROFILM CORROSION RESISTANT COATING

CROSBY VALVE & GAGE CO. WRENTHAM, MASS.	
SAFETY VALVE FOR CHLORINE SERVICE METALLIC SEAT DESIGN	
STYLE 1/2 JQ 225 (DWG. D-13105) 1/2 JQ 375 (DWG. D-38615)	DRAWING NO. H-51970 REV A

steel with two layers of 5 cm cork for insulation and 0.3 cm steel jacket on the outside. The steel should not crack on impact, but rather deform. Strain introduced in this manner should not significantly accelerate corrosion, and the outside of the tank car should degrade rather slowly, of the order of 0.5 mm per year [2]. Corrosion will not take place on the inside of the tank cars provided water does not leak in, since a protective chloride layer is formed by the interaction of the chlorine and iron. The cars are quite rugged, and it is reported that when two cars fell down an incline east of Prince George, B.C., one car punctured the other, but the second car survived the fall and was retrieved intact.

The most vulnerable area for corrosion is around the hot rolled monel valve seat. How quickly this could cause penetration depends very strongly on how well the valve body and steel were coated with paint. A minimum time of two to three years has been estimated, while 10–20 years is more likely [2]. Once a pinhole is formed it should expand rapidly since the acidic chlorine water mixture is quite corrosive. A second place where leakage could occur is in the Crosby safety valve. Figure 1 shows a detailed schematic of the valve used for chlorine service on North American tank cars. The upper diaphragm will not stand more than 3.5 bars external pressure, and water could penetrate between the safety valve seat and disc [3]. Since rupture is inevitable it was decided to examine aspects of the chlorine–seawater system in order to predict the likely sequence of events following tank car failure.

The study was initiated by a literature search out of which the appropriate phase diagrams have been constructed. Further, the likely speciation of chlorine and its effects on pH, alkalinity, and pE have been estimated. In order to fill in gaps in our knowledge of the behavior of chlorine in the marine environment we ran some chlorine demand experiments on seawater and surface sediment from the Strait of Georgia. In order to test the thermodynamic predictions in the field we also carried out some small scale chlorine releases at various depths in the water column from the submersible, Pisces IV.

Thermodynamics

Phase diagrams

The phase diagram for the chlorine-water mixture forms a three dimensional system with the variables composition, pressure and temperature. Figures 2–5 present some two dimensional aspects of the phase diagram which cover conditions likely to be encountered in the region where the tank cars were lost.

In order to calculate the position of the lines on each phase diagram, data was extracted from Ketelaar [4] for the chlorine rich side, and from Fernandez et al. [5] for the remainder of the diagram. Vapor pressures of chlorine were drawn from the Matheson Gas Data Book [6]. In making the various equilibrium calculations, it was assumed that only a two component system existed, that is, seawater with a salinity of 35‰ and chlorine. (Salinity is defined as the weight of inorganic salts in one kilogram of seawater

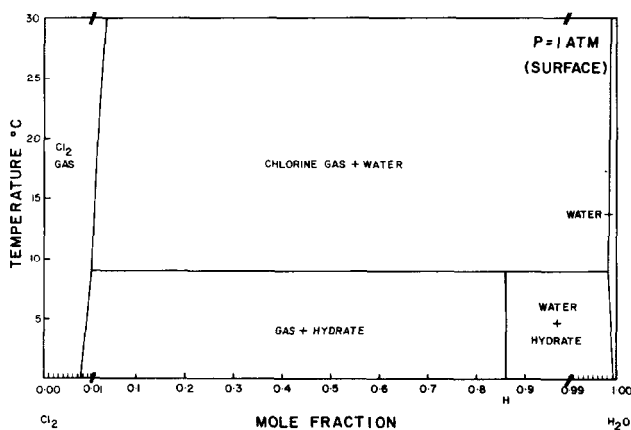


Fig. 2. The phase diagram for the chlorine-seawater system at 1 bar pressure (surface).

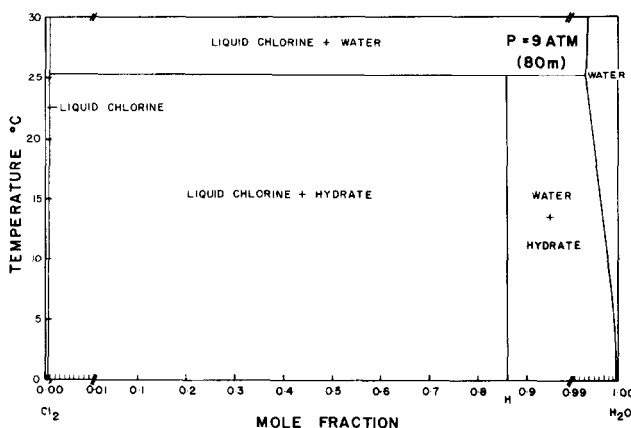


Fig. 3. The phase diagram for the chlorine-seawater system at 9 bars pressure (80 meters depth).

when all bromides and iodides are replaced by an equivalent quantity of oxides. Most of the salinity is made up from contributions by a few major ions. In seawater of 35‰ (35 per mille or 35 parts per thousand) there are approximately 19.3 g of Cl⁻, 10.8 g of Na⁺, 2.7 g of SO₄²⁻, 1.3 g of Mg²⁺ and 0.4 g each of Ca²⁺ and K⁺. Therefore the calculations cannot be rigorously applied to the case where other atmospheric components such as nitrogen and oxygen are included. If an atmosphere of fixed composition was also included, there would be four dimensions on the phase diagram and the possibility of a gas phase even at high pressures. This does not limit the utility of the phase dia-

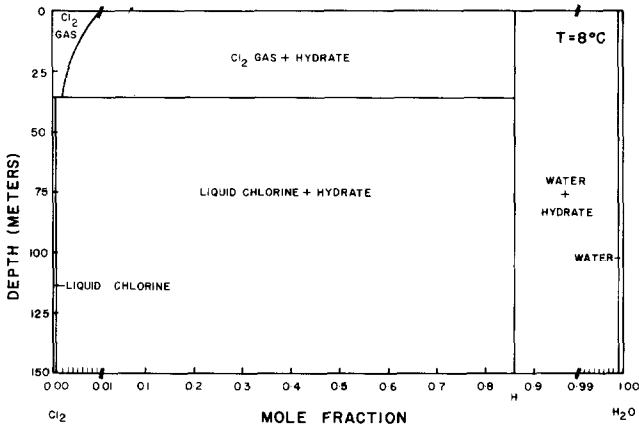


Fig. 4. The phase diagram for the chlorine—seawater system at 8°C.

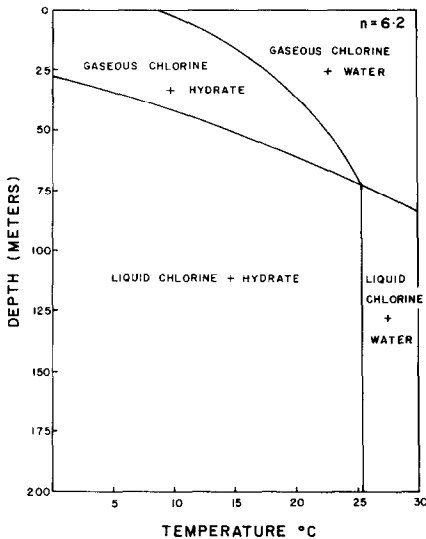


Fig. 5. The phase diagram for the chlorine—seawater system at the hydrate composition.

grams since, as a first approximation, chlorine and seawater mixtures below the surface are essentially isolated from the atmosphere. With an unlimited volume of atmosphere in intimate contact with the chlorine—water system it is expected that the chlorine would partition into the atmosphere according to its vapour pressure over water. This may be considered as a possible removal path of chlorine from seawater. Chemical reactions in the water column will also lead to chlorine removal.

A brief description of how the phase diagrams were calculated is included here in order to clarify the estimates and assumptions which have been made. In considering water solubility in liquid chlorine, chlorine solubility in water and the composition of the hydrate, it is assumed that over a range of 0–20 bars, hydrostatic pressure does not cause any appreciable effects. It is also assumed that hydrostatic pressure does not significantly alter vapour pressure. It can be shown that this is justifiable since:

$$\frac{dP}{dP_s} = \frac{\bar{V}_{\text{liquid}}}{\bar{V}_{\text{vapour}}} \quad (1)$$

where P is vapour pressure, P_s is the total pressure (including hydrostatic and other contributions) and the \bar{V} 's are the respective molal volumes. For water vapour, increasing the total pressure from 1–10 bars results in less than a 1% increase in vapour pressure. Vapour pressure for water over seawater (35‰) were taken from Sverdrup, Johnson and Fleming [7]. The mole fraction of water in the saturated gas phase was estimated as:

$$\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}} + P_{\text{Cl}_2}} \cong \frac{P_{\text{H}_2\text{O}}}{P_{\text{Cl}_2}} = X_{\text{H}_2\text{O}} \quad (2)$$

Vapour pressure of water over hydrate was estimated from the data of Ketelaar [4].

Equilibrium between chlorine gas and water was calculated from the data of Bozzo in Fernandez et al. [5] on chlorine solubility in NaCl–water solutions at various pressures and temperatures (a salting out coefficient for 35‰ seawater based on NaCl solutions was calculated to be about 0.7). Chlorine solubilities in the hydrate region were obtained from Bozzo's Fig. 7 in Fernandez et al. [5]. The solubilities of chlorine in water outside the hydrate region at 9 bars pressure were extrapolated for various temperatures from Bozzo's Table IV taking into consideration the salting out effect.

The solubilities of water in liquid chlorine were taken from the data provided by Ketelaar [4] for both the liquid water and hydrate region. Here it was assumed that the influence of salt on the activity of liquid water was negligible (this assumption is quite acceptable since the activity of the water is directly related to its vapour pressure, and only a relatively small vapour pressure lowering is observed in going from distilled water to seawater).

Fernandez et al. [5] determined that the formula for chlorine hydrate was $\text{Cl}_2 \cdot 6.2\text{H}_2\text{O}$ and this composition has been assumed for the phase diagrams presented here. Their measurements also show that the quadruple point is at 28.3°C and a pressure of about 8.1 bars. Salt depresses the temperature of the invariant point, and this effect has been taken into consideration.

Implications of the phase diagram

Using the phase diagram a possible sequence of events can be predicted given

the depth of water and the temperature. Since the phase diagrams are based on equilibrium calculations, conclusions can only be drawn as to what is possible, or thermodynamically acceptable. Other aspects such as very slow kinetic behavior may prevent thermodynamic equilibrium from being obtained. With this in mind, let us consider two possibilities, a spill at the surface (1 bar pressure) and a spill at 80 meters (9 bars).

Figure 2 shows that at 1 bar, pure chlorine can form a gas over the whole range of temperature from 0–30°C. On mixing the chlorine into about 0.01 mole% water there will be a possibility of obtaining a solid hydrate if the temperature is below about 8°C. Further dilution with water will not result in any phase change until the molar ratio of water to chlorine exceeds 6.2 : 1 at which point a water phase in equilibrium with the hydrate is possible provided that temperature is low enough. Eventually, when the mole fraction of the water exceeds 0.998, only a water phase will be present with some dissolved chlorine forming a seawater “bleach”. This will occur when there are 10g or less of chlorine dissolved in 1 liter of seawater.

Figure 3 shows that at the 9 bars pressure one does not expect a gaseous phase over the 0–30°C temperature range. Following the dilution path of chlorine, a liquid chlorine phase is expected initially. With sufficient water the hydrate will start to form (below 26°C) or chlorine and liquid water will coexist above that temperature. Further dilution will eventually result in dissolution of the hydrate or liquid chlorine. Since the bulk of seawater in Malaspina Strait is at or near 8°C [8] reference to Fig. 4 will give a rough idea of the various possibilities. Only in a very small region is the gas phase possible, and it is anticipated that initially liquid chlorine and hydrate will occur (below 40 m) and after dilution only hydrate and water would be thermodynamically stable. Eventually all hydrate would dissolve given sufficient water.

Chlorine release experiments

On August 20, 1976, some small scale chlorine release experiments were performed in Saanich Inlet, B.C. at a series of depths from 145 m to 25 m. A small cylinder (10 cm diameter × 36 cm length, Canada Liquid Air) was half filled with liquid chlorine and padded to 35 bars with nitrogen. The outlet was connected through a short length (1 meter) of 0.3 cm OD stainless steel tubing, acting as a flow restrictor, to a Whitey ball valve. After the ball valve, a short piece of 0.6 cm stainless steel tubing was connected with a one-way check valve at the end, and a short piece of 0.6 cm OD teflon was connected last (Fig. 6). The ball valve was opened and closed by a Whitey hydraulically operated valve actuator with spring return. The actuator was connected through a hydraulic reduction valve (14 bars) to the Pisces Hydraulic system (69 bars) which was operated from within the Pisces.

During the release experiments visual examination, colour 35 mm slides and “super 8” movies were used to document the behavior of chlorine at various depths when released into water. In the following description it will be assumed that every 10 meters depth of seawater is approximately equivalent to 1 bar pressure so that, for example, 80 meters would have a total pres-

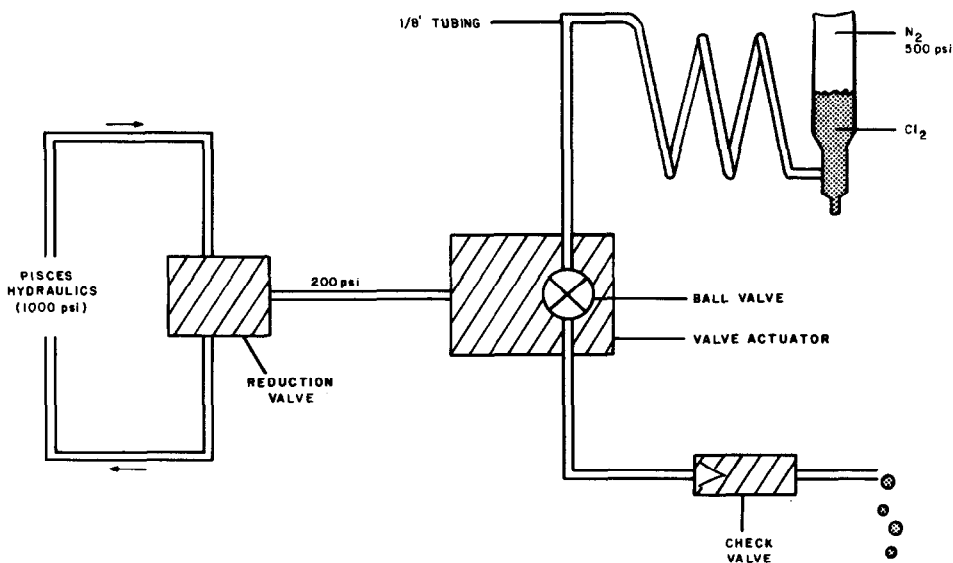


Fig. 6. Schematic diagram of the equipment used to release small amounts of chlorine from the "Pisces" at various depths.

sure of 9 bars, atmospheric pressure being included. This should not be in error by more than about 2%. Accurate interconversion of pressure and depth can be made provided salinity and temperature data are available [9]. Water temperature below 25 meters was between 8° and 11°C.

At 145 meters (15.7 bars) chlorine emerged from the tube as a thick syrup-like fluid, some running down the tube, and some squirting into the water column and then quickly descending in drops about 0.5 cm in diameter (Fig. 7). No hydrate was seen although the chlorine rapidly disappeared from sight below the "Pisces" viewing ports before mixing to any degree with the water.

At 90 meters the chlorine entered the water more vigorously (due to reduced hydrostatic pressure) and could be observed for a longer time period than before. Figure 8 shows liquid chlorine drops in the water column. Some hydrate can also be seen forming on a few of the drops, and fine white flakes of hydrate were clearly seen, dispersed through the water a short time after the chlorine has been released. These flakes appeared to have almost neutral buoyancy neither rising nor falling at an observable rate. The density of the hydrate is 1.23 g/ml which indicates that it could eventually sink at a rate dependant on particle size. Further up in the water column chlorine existed in a much more turbulent plume, and hydrate formed more rapidly than before. At 45 meters some gaseous chlorine was seen attached to hydrate clumps causing them to rise, and for a short time chlorine, hydrate, and gaseous chlorine existed simultaneously. Fine flakes of hydrate were again witnessed shortly after the release (Fig. 9). At 25 meters no liquid chlorine was observed, and the chlorine formed a gaseous phase (Fig. 10). Since liquid

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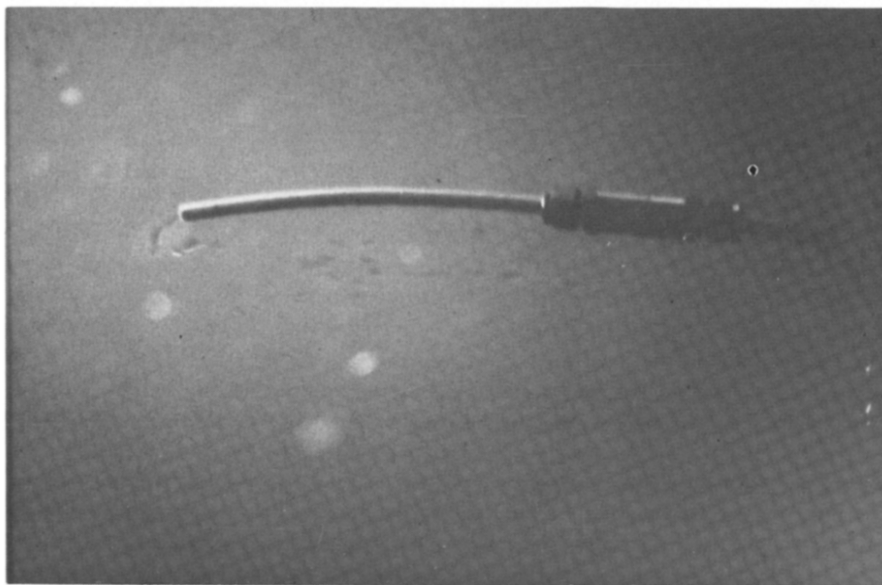


Fig. 7. Liquid chlorine drops sinking in seawater at a depth of about 145 meters.

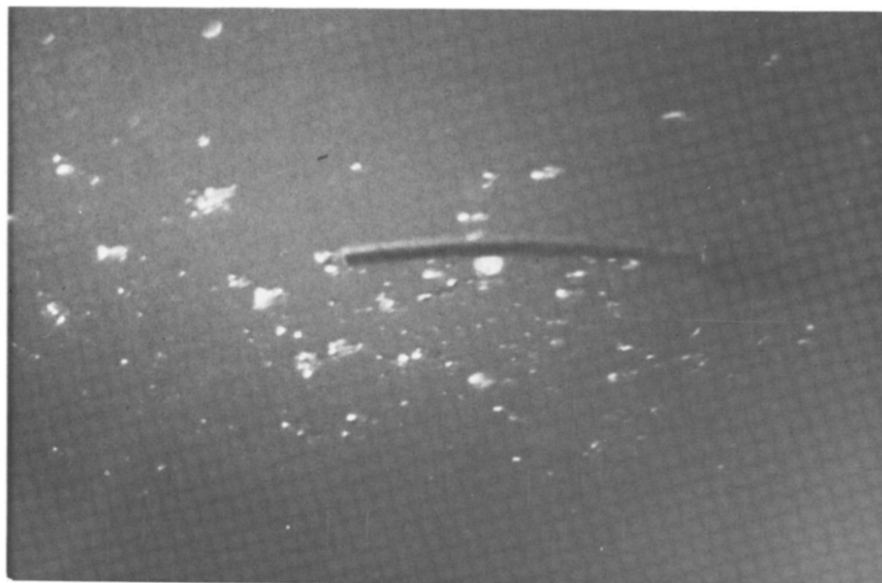


Fig. 8. Liquid chlorine and hydrate sinking in seawater at a depth of about 90 meters.

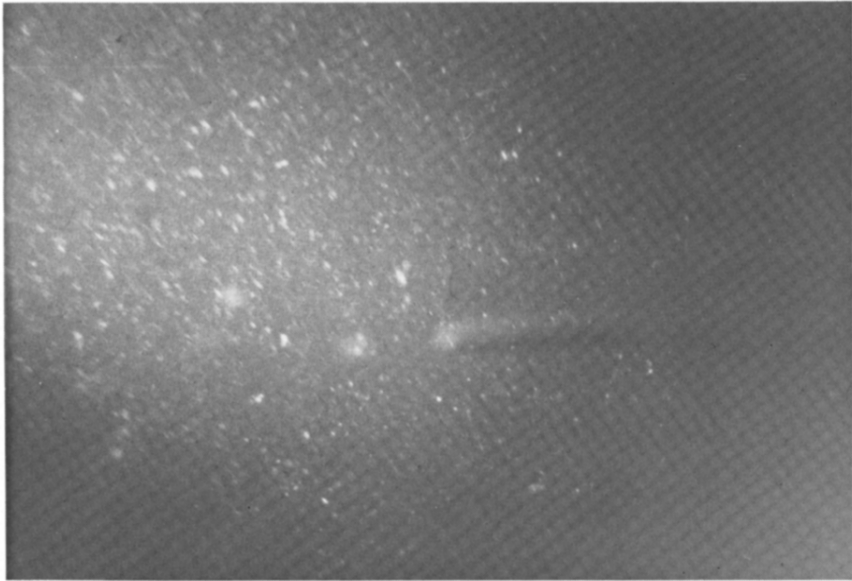


Fig. 9. Fine flakes of hydrate generated shortly after chlorine release at the 45 meters depth. Similar flakes were seen at the 60 and 90 meters depths.

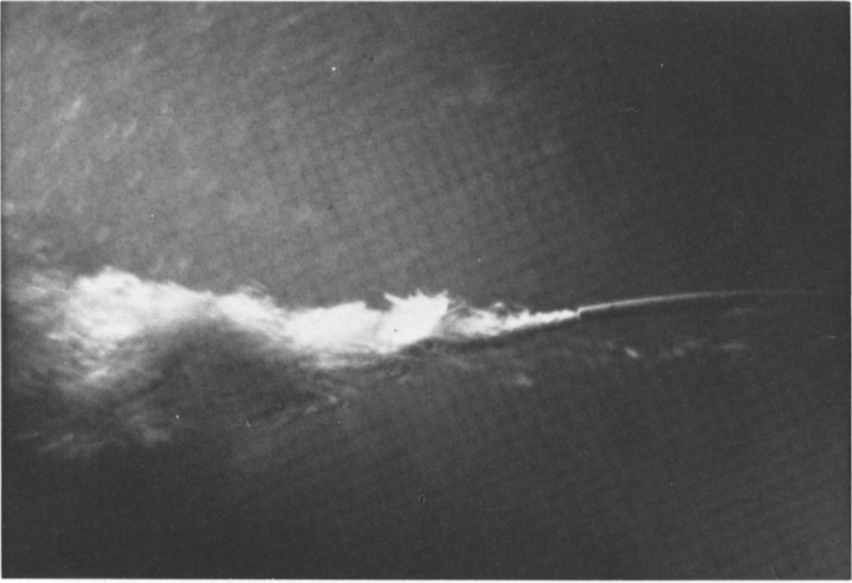


Fig. 10. Plume of gaseous chlorine at the 25 meters depth.

chlorine remained in the bottle at the end of the experiment, this gas was not coming directly from the bottle, but was forming from liquid chlorine as it encountered reduced pressure on leaving the bottle. An observer at the surface did not detect any odour of chlorine even though several discharges were made at the 25 meters depth. Some gas bubbles were seen at the surface, but only after the *Pisces* had cleared her ballast tanks.

The physical behavior of chlorine conforms quite closely with thermodynamic prediction (Figs. 2–5), gas forming above about 45 meters, and hydrate clumps rise due to the attached bubbles above that depth. Below 45 meters at 8–10°C liquid chlorine and hydrate are stable until dilution results in their eventual dissolution.

Turbulent mixing appears to favour hydrate formation, an observation consistent with the conclusions of de Graauw and Rutten [10] who found hydrate production to be transport controlled with the slowest step occurring at the chlorine–water interface.

Enthalpy of the chlorine–water system

On mixing chlorine with water there is a possibility of removal or addition of heat as a result of reactions. Highly exothermic reactions are of importance since they could induce thermal plumes in the water column, or alter the temperature locally causing a different result than thermodynamics based on water temperature would predict.

Table 1 lists the reactions likely to occur when chlorine and water are mixed, and the respective enthalpy changes. The ΔH 's are based on pure water solutions at 25°C [11]. Figure 11 shows systematically the enthalpy levels referenced to liquid chlorine. A quick glance shows that the majority of the immediate reactions are endothermic, with only the formation of aqueous Cl_2 being slightly exothermic. The solubility of the hydrate at 10°C is less

TABLE 1

Enthalpies of chlorine–seawater system at 25°C

Reactions	$\Delta \bar{H}$ (kcal/mole)
$\text{Cl}_2(\text{g}) \rightarrow \text{Cl}_2(\text{l})$	–4.3
$\text{Cl}_2(\text{g}) \rightarrow \text{Cl}_2(\text{aq})$	–5.6
$\text{Cl}_2(\text{l}) \rightarrow \text{Cl}_2(\text{aq})$	–1.3
$\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl} + \text{HClO} (\text{conc.})$	3.3
$\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl} + \text{HClO} (\text{dilute})$	–0.6
$\text{Cl}_2(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl} + \text{HClO} (\text{conc.})$	7.6
$\text{Cl}_2(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl} + \text{HClO} (\text{dilute})$	3.7
$\text{Cl}_2(\text{g}) + n\text{H}_2\text{O}(\text{l}) \rightarrow \text{Cl}_2 \cdot n\text{H}_2\text{O}(\text{s})$	16.6
$\text{Cl}_2(\text{l}) + n\text{H}_2\text{O}(\text{l}) \rightarrow \text{Cl}_2 \cdot n\text{H}_2\text{O}(\text{s})$	20.9
$\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HCl} + \frac{1}{2}\text{O}_2(\text{aq})$	–13.2
$\text{Cl}_2(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HCl} + \frac{1}{2}\text{O}_2(\text{aq})$	–8.9
$\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{aq})$	–3.3

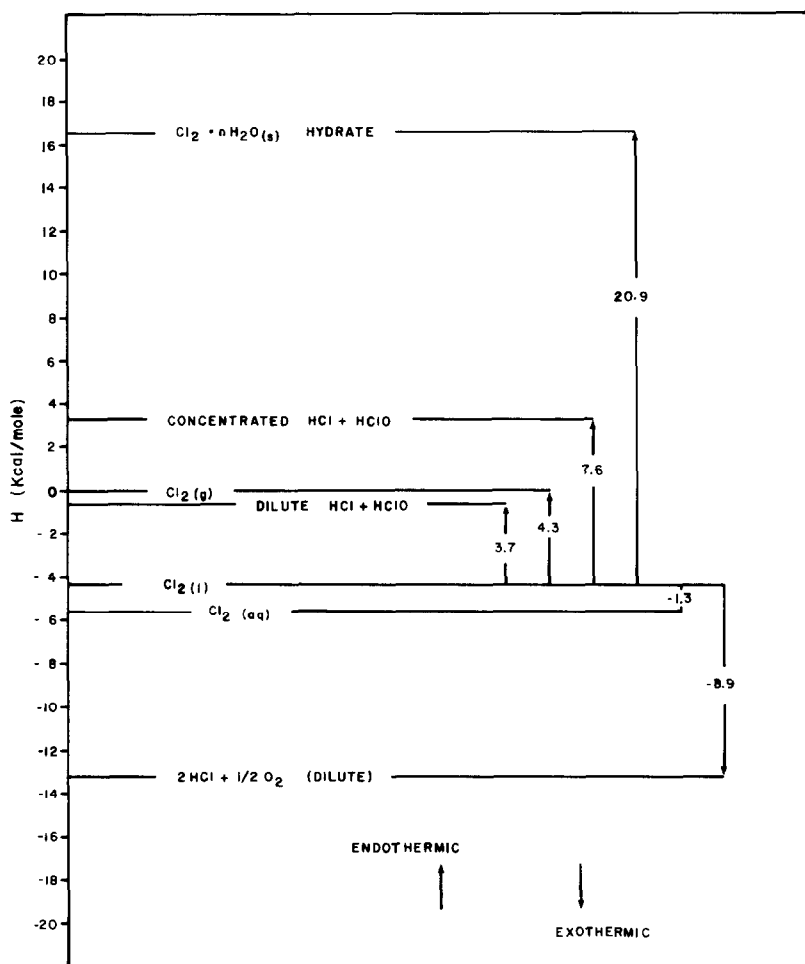


Fig. 11. The ΔH changes (referenced to liquid chlorine) when chlorine undergoes phase changes or reacts with water at 25°C.

than 10 g/l. Assuming that liquid chlorine and water formed a hydrate which subsequently dissolved to form Cl_2 saturated water, a temperature rise of about 0.2°C is possible. The reaction to form $\text{HCl} + \text{O}_2$ can release about 8.9 kcal/mole when starting with liquid chlorine and water, but this reaction is not fast and could take up to years in the dark without catalysts. When liquid chlorine and water are mixed it is expected that the temperature will drop slightly at first due to the hydrate formation, but will eventually rise slightly as the hydrate dissolves. Decomposition of HClO could release some energy but only at a very slow rate, or after significant dilution. Temperature changes resulting from chlorine—water mixtures will therefore be very minimal.

Gaseous explosions

When a liquified gas is spilled onto or injected into a second fluid, there is a possibility of forming superheated drops where the temperature of the drops is elevated above the normal boiling point.

Under the usual circumstances when a liquid exposed to a gas phase is raised to its boiling point it will simply boil at a constant temperature. Bubble formation during boiling results from nucleation on the walls of the vessel, or from impurities in the boiling liquid where microscopic irregularities trap or absorb gas and present a gas-liquid interface where a bubble can be formed. Kinetic analysis shows that the probable formation of a bubble within a liquid (homogeneously) at the normal boiling point is very low.

If a drop of liquid gas is placed into another fluid at a temperature in excess of the boiling point of the liquified gas, the drop can remain stable even at remarkably high temperatures. For example several authors have been able to reproducibly heat n-pentane to 146–147°C at atmospheric pressure [12]. This is over 100°C in excess of its normal boiling point. There is, however, a definite limit to which a liquid can be heated called the “superheat” or “cavitation” limit, above which an explosion can take place. Since the boiling point of chlorine is –34.5°C at atmospheric pressure, and the water temperature in Georgia Strait may be expected in the 5–15°C temperature range, the injection of liquid chlorine into the water could result in superheated drops. It is important to ascertain the likelihood of an explosion or explosions following the rupture of a tank car submerged in water. This discussion applies only to the range of depths where gas is thermodynamically stable (at depths deeper than 50 meters when liquid chlorine is stable, explosions will never be a problem).

Thermodynamic stability analysis shows that for a pure liquid superheat limit occurs when [13]:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad (3)$$

Using this criterion and the Redlich-Kwong [14] equation of state, Reid [12] has provided a generalized curve of reduced pressure $\frac{P}{P_c}$ as a function of

the reduced superheat limit $\frac{T_{sl}}{T_c}$ where P_c and T_c are the critical pressure and

temperature respectively. This curve gives an adequate representation of experimental observations on many gases. Based on this curve and the critical temperature and pressure of chlorine (417 K, 76.8 bars) the water temperature would have to be close to 100°C before explosion could take place at atmospheric pressure, a situation not likely to occur in Georgia Strait.

Chlorine in the marine environment

Speciation

Chlorine reacts with water very quickly to form hypochlorous acid which can then further dissociate:



The equilibrium constant for eqn. 4 has been measured by the least two groups and they have been reviewed by White [15]. At 8°C:

$$K_H = \frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]} = 2.4 \times 10^{-4} \quad (6)$$

The dissociation of hypochlorous acid in seawater has recently been studied and the apparent ionization constant K'_i has been given as a function of salinity and temperature [16]:

$$K'_i = \frac{[\text{OCl}^-_t] a_{\text{H}}}{[\text{HOCl}]} \quad (7)$$

where OCl^-_t is the total concentration of hypochlorite, and a_{H} is the operational hydrogen ion activity obtained from a pH measurement with a glass electrode and a reference electrode with liquid junction.

Consideration simultaneously of both eqns. 4 and 5 allows one to calculate the equilibrium concentration of the chlorine species as a function of pH. The ratio of each species to the total chlorine present is shown in Fig. 12 where:

$$\alpha_0 = \frac{[\text{Cl}_2]}{[\text{Cl}_2] + [\text{HClO}] + [\text{ClO}^-_t]} \quad (8)$$

$$\alpha_1 = \frac{[\text{HClO}]}{\Sigma \text{Cl}_2} \quad (9)$$

$$\alpha_2 = \frac{[\text{ClO}^-_t]}{\Sigma \text{Cl}_2} \quad (10)$$

Consideration has been taken of the chloride concentration in seawater which tends to shift eqn. 4 to the left on going from freshwater to seawater. Figure 12 shows that ClO^-_t comprises 10% or more of the chlorine species in seawater only when the pH is above 6. From pH 4 to 6 HClO is the dominant form, while dissolved aqueous chlorine becomes significant below pH 4.5.

Oxidation reactions involving HClO or ClO^- can also liberate protons which no longer have an associated chlorine species as shown by eqn. 11.



The effect of chlorine on alkalinity and pH of seawater

According to eqn. 4 the addition of Cl_2 to seawater can be considered as a titration of seawater with strong acid. Protons can also be added through the secondary ionization of HOCl (this secondary reaction will affect pH but not titration alkalinity since for each mole of proton added, one mole of the conjugate base OCl^- is also added. Titration to a pH of 4 endpoint will cause

TABLE 2

Selected properties of the chlorine—seawater system

		Refs.
<i>Chlorine</i>		
Molecular weight	70.9 g/mole	6
Boiling point	-34.5°C	6
Specific gravity 0°C	1.47	6
Specific gravity 25°C	1.41	6
Specific heat (l)	0.226 cal/g	6
Specific heat (g) Cp	0.114 cal/g	6
<i>Chlorine hydrate</i>		
Composition (Cl ₂ · nH ₂ O)	n=6.2	5
Critical decomposition temp.	28.3°C	5
Specific gravity	1.23	36
<i>Seawater</i>		
Density (33‰, 8°C)	1.026	37
Density (15‰, 5°C)	1.011	37
Specific heat (33‰, 8°C)	0.956	38
Specific heat (15‰, 15°C)	0.979	38

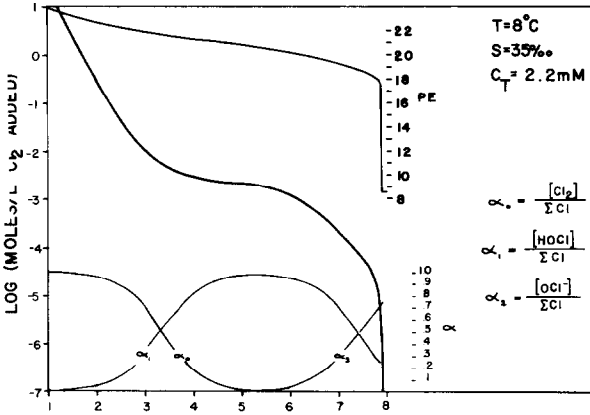


Fig. 12. The speciation of chlorine in seawater as a function of pH. Shown also is the titration curve expected when chlorine is added to seawater at 8°C with an initial pH of 7.9 and a total carbonate concentration of 2.2×10^{-3} mole/l. The redox potential as a function of chlorine added for 25°C is also drawn in at the top of the diagram.

all the OCl^- to be converted back to HOCl . Oxidation reactions removing OCl^- will of course lower the alkalinity).

In the long term, once all the active species have been reduced to chloride, two moles of H^+ will have been generated for each mole of Cl_2 added to seawater. If we accept an alkalinity change of 2% or less as being relatively insignificant, the 296 metric tons of chlorine contained in the tank cars will have to be diluted by about $2 \times 10^8 \text{ m}^3$ of seawater.

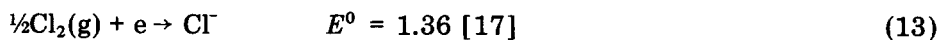
Let us now consider the influence of adding Cl_2 to seawater on the pH of seawater. A "typical" sample of seawater might have a total CO_2 of about $2.2 \times 10^{-3} \text{ mole/l}$ and a pH of 7.9. Using the apparent dissociation constants for the CO_2 system [17] and K_w^{SW} for seawater [18] for 8°C and 35‰ salinity, it is possible to estimate what addition of strong acid is required to cause the pH to change to any specified values in a closed system (i.e. CO_2 is not allowed to escape to the atmosphere). Titration with chlorine has the added complexity that an aqueous chlorine species is possible. Using the appropriate equilibrium constants [15,16] corrected to 8°C the titration curve for the "typical" seawater has been estimated and is included on Fig. 12 along with the speciation of chlorine. The interesting features are that at high pH (6.5–7.9) the system is buffered to a certain extent by OCl_t^- particularly at about pH 7.2 when $[\text{OCl}_t^-] = [\text{HOCl}]$. The pH therefore does not change as rapidly in this region with the addition of chlorine as it does when most of the OCl^- is converted to HOCl below pH 6. Below pH 3.5 aqueous Cl_2 becomes an important species since the equilibrium of eqn. 4 is shifted to the left. Addition of large amounts of chlorine here do not have a great influence on the pH. Of course at high additions of chlorine other phases will become possible, such as hydrate or liquid chlorine, at which point the titration curve must break down.

Effect of chlorine on redox potential of seawater

The redox potential of a system at equilibrium is expressed as a dimensionless quantity pE. Analogous to pH, pE is the negative logarithm of electron activity. It is referenced to a conventional zero assigned to the standard hydrogen electrode.

$$\text{pE} = -\log\{e\} = \frac{F Eh}{2.3 RT} = \frac{Eh}{0.059} \quad (12)$$

where F is the Faraday, R the gas constant and T the absolute temperature, and Eh is the half cell potential corrected for concentration. Redox potential is normally discussed in terms of both pE and Eh , the interrelation being demonstrated in eqn. 12. For oxic seawater the measured pE is found to be approximately 8.5 suggesting that the pE is controlled by the $\text{O}_2/\text{H}_2\text{O}_2$ couple [19]. Addition of chlorine to seawater is expected to upset the precariously poised system, chlorine being a strong oxidant. If it is assumed that the seawater becomes controlled by the Cl_2/Cl couple then:



From fundamental thermodynamics:

$$\Delta G = -\eta FE^0 = -RT \ln K \quad (14)$$

where ΔG is the standard free energy change and K is the equilibrium constant associated with the respective reaction. For eqn. 13:

$$\log K = \log \left[\frac{\{Cl^-\}}{P_{Cl_2}^{1/2} \{e\}} \right] = \log \{Cl^-\} + pE - \frac{1}{2} \log P_{Cl_2} \quad (15)$$

For seawater of 35⁰/₀₀ salinity:

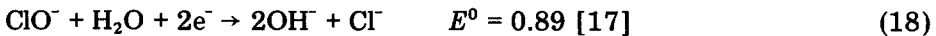
$$\{Cl^-\} = [Cl^-] \gamma_{Cl^-} = 0.55 \times 0.66 = 0.36 \quad (16)$$

(γ_{Cl^-} was taken from Whitfield [20])

$$pE = 23.5 + \frac{1}{2} \log P_{Cl_2} \quad (17)$$

Variation of P_{Cl_2} from 0.1 to 10 bars will not cause a large change in pE and therefore $pE = 23.5$ should be a good estimate when the couple in eqn. 13 controls redox potential. Reversing the procedure, it obtains directly from eqn. 17 that normal oxic seawater with pE of 8.5 has a negligibly small P_{Cl_2} of about 10^{-30} atmospheres.

Perhaps a more useful way of looking at the redox potential of chlorinated seawater is to consider the hypochlorite ion:



Taking K_W^{sw} for 25°C from Culberson and Pytkowicz [18] and estimating the activity of water in seawater from vapour pressure lowering [7] it can be shown that:

$$pE = 28.5 - pH + \frac{1}{2} \log \{ClO_t^-\} \quad (19)$$

Using the approximation given by Sugam and Helz [16] for the activity coefficient of the hypochlorite ion in seawater:

$$pE = 28.4 - pH + \frac{1}{2} \log \{Cl_t^-\} \quad (20)$$

Eqn. 20 is simply a different formulation of eqn. 17, but it is easier to see the influence of chlorine on pE because by reference to Fig. 12 it is possible to estimate pH. The effect of chlorine added to seawater on pE (25°C) is also shown on Fig. 12.

Eqns. 17 and 20 are also useful for determining the oxidation state of the elements in seawater at equilibrium, and for instance, it can be shown that bromide should be converted to bromine at equilibrium in the presence of chlorine.

The chlorine demand of seawater and sediment

So far we have examined the immediate interaction of chlorine with sea-

water, and what effect it will have on such seawater parameters as *Eh*, pH, alkalinity and temperature. A second and equally important question is where will the chlorine go in the short term and the long term? In the aquatic environment there are a variety of removal paths through which chlorine can be lost. Given sufficient time and mixing all the chlorine with a +1 valence will eventually be removed through redox reactions. A variety of components naturally present in seawater will be important for chlorine removal some of which are listed below [15]:

1. Ammonia
2. Amino Acids
3. Proteins
4. Organic Carbon
5. Nitrite
6. Iron
7. Manganese
8. Sulphide

Many of the listed compounds are produced and regulated by biological processes and are contained in dead or living material. The most important group of compounds with regard to the short term chlorine interactions are those containing nitrogen, especially ammonia which leads to the formation of chloramines:



The above are not redox reactions in that chlorine still maintains its +1 valence and these compounds still have oxidizing, disinfecting and biocidal capacity. An excellent and complete review of the interaction of chlorine with ammonia and other compounds is given by White [15] to which the reader is referred for more detail than is provided here. Jolley [21] has also collected much data on the speciation and exchange reactions involving chlorine in water.

Chlorine which is tied up by ammonia or nitrogen compounds is known as "combined available chlorine residual" or just "combined residual". Residual chlorine existing as hypochlorite ions or hypochlorous acid is termed "free available chlorine residual" or "free residual" [22]. In addition to the interaction of chlorine with nitrogen compounds, other reactions are possible with the substances listed above. Reducing agents such as H_2S , Mn^{2+} , Fe^{2+} and organic carbon can be oxidized and so remove the chlorine quickly from the water. Loss of chlorine in this manner is referred to as the "chlorine demand" of the water [23]. Chlorine demand, then, is that amount of chlorine which the water can remove by reducing the Cl^{+1} to Cl^{-1} or by irretrievably tying up

the chlorine in some organic compound. Operationally, demand is defined as the "difference between the amount of chlorine applied and the amount of free, combined or total available chlorine remaining at the end of a contact period" [24].

With respect to chlorination, seawater has one important difference to fresh water, it contains an appreciable quantity of bromide, with 67.3 mg/kg in seawater of 35‰ salinity [25]. Chlorine will displace this bromide. The bromine produced in this manner is then free to react in an analogous manner to chlorine producing hypobromous acid and bromamines. Most instrumental methods do not differentiate bromine and chlorine contributions, and therefore seawater measurements have been commonly referred to in terms of chlorine demand [26]. In the remainder of this report we will refer to all measurements in terms of chlorine, tacitly realizing that some bromine or brominated species will be contributing.

Griffin [27] in experimenting with higher than normal residuals used for water treatment discovered the so called "breakpoint" phenomenon. Measured chlorine residuals initially increase with the amount of chlorine added but, after sufficiently large dose, drop off. This behaviour is caused by the interaction of chlorine and ammonia. After the minimum or breakpoint, free residual chlorine can be measured.

A breakpoint curve was determined for some 2 m seawater obtained in Howe Sound from the ship MV Pandora II in July, 1976. Various amounts of chlorine were added to the seawater and the total residual was determined amperometrically after 30 minutes (the amperometric determination of free and combined residual chlorine is well documented by the ASTM handbook [22] and the Fisher and Porter Instruction Bulletin for the amperometric titration made by the company. This titration does not distinguish bromine from chlorine). Figure 13 shows the essential features of the seawater breakpoint curve. Duursma and Parsi [26] in some very recent investigations measured the interaction of ammonia and chlorine in seawater with relatively high doses of both Cl_2 and NH_3 (up to 710 mg/kg Cl_2). Their experiments point out some fundamental differences between the formation of chloramines in seawater and fresh water. It would appear that the breakpoint in seawater is obtained at lower ratios of chlorine to ammonia than in fresh water, and that dichloramine does not persist in detectable quantities.

Taras in his investigation of the chlorine demand of water as a function of time found the empirical relationship [28,29]:

$$D = kt^n \quad (24)$$

where D is the chlorine demand, t is contact time, and K and N are constants determined experimentally. The exponent n relates to the speed of the chlorine consuming reactions, and helps to define the type of compounds which are responsible for removing chlorine.

The higher the exponent, the slower the reaction, and generally the more complicated the reacting species.

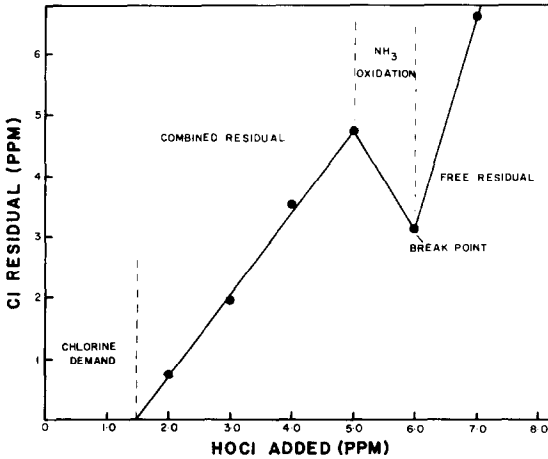


Fig. 13. The breakpoint curve for chlorination of some surface Strait of Georgia water.

Some experiments were run on the chlorine demand of seawater as a function of time on samples obtained in August, 1976, from Saanich Inlet. The chlorine demand was measured for a time period 2 days after an initial dose of 5 mg/l of chlorine on both 30 m and 2 m seawater. Both water depths had a similar behaviour and the 30 meter results are shown in Fig. 14. The exponent of t was found to be 0.22 for the 30 m sample and 0.20 for the 2 m sample indicating that other compounds as well as ammonia are probably responsible for some of the chlorine demand of seawater. Water with the nitrogen component consisting mainly of ammonia has exponents in the 0.01–0.08 range [15].

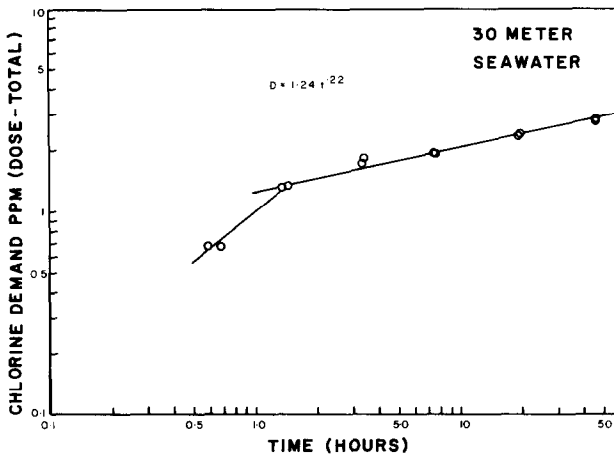


Fig. 14. The chlorine demand as a function of time for some 30 m seawater obtained in Saanich Inlet.

The chlorine demand of some surface sediment obtained from the Strait of Georgia was also measured as a function of time by placing 5.2 g (wet weight) of sediment in a stirred 5 liter flask filled with demand free water which was then chlorinated to 5 mg/l. The exponent of t was found to be 0.28, and the sediment had fairly high demand removing all the chlorine from the 5 liter flask within four hours.

All the chlorine demand experiments were run under ambient laboratory light in a glass container. There is some disagreement in the literature as to the effect of light on the rate of removal of chlorine in seawater, with one report showing chlorine decay accelerated by a factor of 7 in ambient light [30] while another found no difference [26]. More experiments will be required to sort out this discrepancy, but at present it can safely be said that the reaction proceeding in the dark should be no faster than those proceeding under ambient light conditions but possibly as fast. In strong sunlight at the surface, there might be an effect on the removal of chlorine, however for deeper water it is expected that light will play no part at all.

Duursma and Parsi [26] extended their investigations to higher doses of chlorine than used in the present studies with concentrations up to 1600 mg/l. They found that under these circumstances a more or less rapid loss of chlorine was often seen with the higher doses during the first few minutes. Aeration augmented the effect and they hypothesized that some of the chlorine may have been removed by gas bubbling. Their investigations with lower doses (below 600 mg/l) do not show this loss. If air-seawater exchange is the cause of their loss, it is not likely to be of great importance for chlorine injected at depth in the seawater column since atmospheric exchange will be prevented.

The experiments run here show that seawater may be expected to have a short term demand of about 1.5 mg/l (Fig. 14) which agrees with the estimate given by White [15] for the 10 minute demand of seawater of 1.5 mg/l. In any event the chlorine demand should not exceed 3 mg/l unless some organic pollution has taken place. If it is assumed that chlorine demand of seawater is around 3 mg/l after several days in the dark, the total contents of the four tank cars can be absorbed by approximately $1.2 \times 10^8 \text{ m}^3$ of seawater if uniform mixing takes place.

Toxicity in the marine environment

The chemistry of chlorine in seawater can be fairly complex, and prediction of reaction products in the natural environment is virtually impossible [31]. In spite of this, it appears that safety limits can be established with a fair degree of confidence.

After water has been chlorinated, only three basic forms need to be considered for toxic effects. Free residual chlorine, combined residual chlorine and apparent demand chlorine. The third form contributes virtually nothing to toxicity provided secondary toxic products are not formed. In a polluted environment this might constitute a hazard [21,32,33] but in a relatively clean area such as Malaspina Strait this should not be a problem.

The combined and free residual chlorine cause almost all the toxic effect in natural waters so that it is important to consider chlorine remaining in both of these forms rather than original dose added [34]. Whether chlorine is in the free or combined state does not seem to greatly matter as far as toxicity is concerned with both exhibiting the same order of magnitude of effect. The concentration of total residual chlorine appears to be both necessary and sufficient to determine toxicity [31,35].

Equally important to the total concentration of available chlorine is the time of exposure. Mattice and Zittel in a very recent and complete review [31] have constructed a most useful dose—time curve for toxicity of chlorine in both fresh water and seawater, where acute and chronic toxicity thresholds have been estimated from a statistical analysis of compiled data. The chronic toxicity threshold they report is 0.02 mg/l. Since the threshold is a statistical creation, we cannot say there will be no effect below this concentration, but we can say that chances of mortality are small, and become smaller the further below the threshold line the total residual chlorine concentration is. These thresholds have been constructed from data on many different species and so tend to represent the safety limit for the most sensitive.

Conclusions

1. Thermodynamics show that four phases may be expected when chlorine and water are mixed; gaseous chlorine, liquid chlorine, chlorine hydrate (solid) and water. With sufficient dilution chlorine will dissolve completely in water forming a "bleach". Above 50 meters gaseous chlorine can form at the anticipated range of temperatures. Since chlorine, chlorine hydrate, and chlorinated seawater are all denser than seawater at a given salinity and temperature, water contaminated by chlorine leakage below 50 meters should tend to fall and remain in deep water. Analysis of the heats of reaction of chlorine with water show that there should not be a significant temperature change resulting from Cl_2 water mixing.

2. Chlorine release experiments show that the chlorine seawater system conforms very well to the thermodynamic prediction, at least for small releases.

3. Chlorine reacts with water to form several species; Cl_2 , HOCl and OCl^- . The equilibrium involving these species will be important in considering the effect of chlorine on pH, alkalinity, and to a lesser extent toxicity.

4. Chlorine solutions in seawater will be strongly oxidizing, and it is expected that some or all of the 67.3 mg/l of bromide will be converted to bromine.

5. Most of the chlorine speciation reactions are rapid, and hydrate formation is very fast being transport controlled. It is therefore expected that given mixing most of the chlorine will form a hydrate which will later redissolve on dilution. Even in shallow water much of the chlorine should be tied up as an hydrate.

6. The chlorine demand of seawater is about 1.5 mg/l (half hour) and about 3 mg/l after 2 days. Dilution of chlorine to 3 mg/l should result in it being

removed by redox process within a couple of days after dilution.

7. Gaseous explosions caused by superheating of the liquified chlorine gas should not be a problem at the anticipated water temperatures.

8. Chlorine is expected to exhibit toxic effect when present above 0.02 mg/l, but should not cause problems below that level. Once the chlorine has been removed by natural demand of the seawater it is effectively out of the system. If the tank cars are in deep water, as is likely, the toxic water should remain at depth until dilution and time remove the chlorine.

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