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Abstract

An examination of the interaction of chlorine and seawater has been made with particular emphasis on those aspects most pertinent to a spill or leak of liquid chlorine in seawater. This has been done in order to be able to predict the results of a rupture of the chlorine tank cars lost in Malaspina Strait early in 1975.

The appropriate phase diagrams have been constructed from information available in the literature, and small scale release experiments from the submersible, Pisces, confirm that the behavior of chlorine when released at various depths conforms rather closely to thermodynamic prediction. Depending on depth or temperature, four phases are possible: liquid chlorine, gaseous chlorine, liquid water (with chlorine dissolved in it), and chlorine hydrate (solid).

Literature data has been used to predict the effect of chlorine on such seawater parameters as alkalinity, pH, and Eh, and the speciation which should occur with various chlorine in seawater mixtures.

Results of experiments performed here show that, at low concentrations (5 mg chlorine/1 seawater) seawater has a natural demand of about 1.5 mg/1 in half an hour, and 3 mg/1 after a day or so. Sediments can also destroy chlorine with 5 g (wet weight) removing 5 mg of chlorine from a liter flask of stirred seawater within four hours.

Consideration of critical data on chlorine, and a review of our release experiments show that gaseous explosion will not occur when liquid chlorine and seawater are mixed under conditions possible in Georgia Straits.

In the event of a chlorine leakage from a tank car resting on the bottom, liquid chlorine and chlorine hydrate will tend to fall being denser than seawater, and stay near the bottom. At depths less than 40 meters it is possible that gaseous chlorine could form. Depending on depth , much of the gaseous chlorine would not reach the atmosphere but would be tied up as an hydrate and remain in the seawater. Eventually after sufficient dilution, the natural chlorine demand of seawater and sediments will remove the chlorine through oxidation reactions. Mixing will help this process. Secondary toxic products formed by chlorination (or bromination) of organics should not be a problem in a clean area such as Malaspina Strait.

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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 (Fig. 1). Although a series of searches was carried out (A.D. O'Connor, March 1975, November, 1976 and others), the exact location of the sunken cars has not as yet been determined. Each tank car carried approximately 94 metric tons[1] of liquid chlorine with a 10% 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 steel with two layers of 5 cm cork for insulation and a 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 .5 mm per year. Corrosion will not take place on the inside of the tank car provided water does not leak in, since a protective chloride layer is formed by interaction of the chlorine and iron. The cars are apparently quite rugged, and it is reported that when two cars fell down an incline east of Prince George, one car punctured the other car, but the second car survived the fall and was retrieved intact (anonymous).

The most vulnerable area for corrosion is around the hot rolled monel valve seat. Small scratches in a good coat of paint would lead to pit corrosion in the iron in close contact with the 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. Once a pinhole is formed it should expand rapidly since the acidic chlorine water mixture is quite corrosive (Carson, 1975). Since rupture is inevitable it was decided to examine the chemical 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 effect on pH and pE have been estimated. In order to fill in gaps in our knowledge of the chlorine seawater system, we ran some chlorine demand experiments in seawater obtained from Saanich Inlet and on surface sediment from the Strait of Georgia.

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[1] SI units are used throughout this report. Conversion factors to other commonly used units are to be found in Table I.

Before relying on thermodynamic predictions we thought it would be worthwhile to carry out some small scale chlorine releases at various depths of the water column to get some visual verification of the behaviour of chlorine in seawater. This was done from the submersible, Pisces IV, in Saanich Inlet.

Thermodynamics

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 Malaspina Strait.

In order to calculate the position of the lines on the phase diagrams, data was extracted from Ketelaar (1967) for the chlorine rich side, and from Fernandez et al (1967) for the remainder of the diagram. Vapour pressures of chlorine were drawn from the Matheson Gas Data Book (1966). In making the various equilibrium calculations it was assumed that only a two-component system existed, that is, seawater (35°/₀₀) and chlorine. Therefore, it cannot be rigorously applied to the case where other atmospheric components such as nitrogen and oxygen are included. If an atmosphere of fixed composition were 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 these phase diagrams 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 chlorine would partition into the atmosphere according to its vapour pressure. 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 below to make clear the estimates and assumptions which have been used.

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

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

where P is the vapour pressure, P_s is the total pressure (including hydrostatic and other contributions) and the $\overline{V}$'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 pressures for water over seawater (35°/₀₀) were taken from Sverdrup, Johnson and Fleming (1942). The mole fraction of water in the saturated gas phase was estimated as

$$\frac{P_{H_2O}}{P_{H_2O} + P_{Cl_2}} \approx \frac{P_{H_2O}}{P_{Cl_2}} = X_{H_2O} \qquad (2)$$

Vapour pressure of water over hydrate was estimated from the data of Ketelaar (1967).

Equilibrium between chlorine gas and water was calculated from the data of Bozzo in Fernandez et al (1967) on chlorine solubility in pure water NaCl solutions at various pressures and temperatures. (A salting-out coefficient for 35°/₀₀ seawater based on the NaCl solutions was calculated to be about 0.7.) Chlorine solubilities in the hydrate region were obtained from Bozzo's Figure 7 in Fernandez et al (1967). 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. Figure 6 summarizes the solubility of chlorine in seawater as a function of pressure and temperature.

The solubilities of water in liquid chlorine were taken from the data provided by Ketelaar (1967) for both the liquid water and hydrate regions. Here it was assumed that the influence of salt on the activity of 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 on going from distilled water to seawater.)

Fernandez et al (1967), using the Miller-Strong method, determined that the formula for chlorine hydrate was $Cl_2 \cdot 6.2\ H_2O$ and this composition has been assumed for the phase diagrams presented here. Roozeboom (1918) gave the upper invariant point for the hydrate (quadruple point) as 28.7°C, and a pressure of 6.08 bars. Recent measurements of Fernandez et al (1967) indicate that the quadruple point should be at 28.3°C with a pressure of about 8.1 bars. The recent data is probably more accurate and so has been adopted here. Salt depresses the temperature of the upper invariant point, and this effect can be taken into consideration by reference to Bozzo's Figure 6 in Fernandez et al (1967). The temperature at which the hydrate becomes unstable at 1 bar was also determined from this source.

Implications of the Phase Diagram

The phase diagram can be used to predict a possible sequence of events if chlorine is injected at some point into the water column. 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 behaviour may prevent thermodynamic equilibrium from being obtained. With this in mind, let us consider two possibilities, a spill at the surface (1.01 bar) and a spill at 80 meters (9 bars).

Reference to Figure 2 shows that at 1 bar, pure chlorine can form a gas phase over the whol- range of temperatures from 0-30°C. On mixing chlorine with water in a mole ratio of 99:1 there will be a possibility of obtaining chlorine gas over a chlorine saturated water solution, or chlorine gas over a solid hydrate (crystalline yellow) if the temperature is below about 8°C. Further dilution with water will not result in any phase changes 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 the temperature is sufficiently low. Eventually, when the mole fraction of water exceeds .998, only a water phase will be present with some dissolved chlorine forming a seawater "bleach". This will occur when there are 10 g or less of chlorine dissolved in 1 litre of seawater.

Reference to Figure 3 shows that at 9 bars pressure one does not expect a gaseous phase over the 0-30° temperature range. Following the dilution path of chlorine, a liquid chlorine phase is anticipated 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.

If the bulk of seawater at Malaspina Strait is at or near 8°C (Crean and Ages, 1968) reference to Figure 4 will give a rough idea of the various possibilities. Only in a very small region is a gas phase possible, and it is anticipated that initially liquid chlorine and hydrate would occur (below 40 m) and after further dilution only hydrate and water would be thermodynamically stable. Eventually all hydrate would dissolve given a sufficient quantity of water.

Speciation

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

$$\mathrm{Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^-} \qquad (3)$$

$$\mathrm{HOCl \rightleftarrows H^+ + OCl^-} \qquad (4)$$

The equilibrium constant for Equation 3 has been measured by at least two groups and their results have been reviewed by White (1972). At 25°C,

$$K_H = \frac{[\mathrm{H^+}]\ [\mathrm{Cl^-}]\ [\mathrm{HOCl}]}{[\mathrm{Cl_2}]} = 4.47 \times 10^{-4} \qquad (5)$$

The dissociation of hypochlorous acid in seawater has recently been examined by Sugam and Helz (1976) and the apparent ionization constant K'_i has been given as a function of salinity and temperature.

$$K'_i = \frac{[OCl^-_t]\ \tilde{a}_H}{[HOCl]} \qquad (6)$$

Where OCl^-_t is the total concentration of hypochlorite, and $\tilde{a}_H$ is the operational hydrogen ion activity obtained from a pH measurement with a glass electrode and a reference electrode with liquid junction. Figure 7 shows the fraction $\frac{OCl^-_t}{HOCl}$ as a function of pH and temperature.

On a recent cruise on the CSS Vector (November 29 - December 3, 1976) a pH profile was determined at two stations. Measurements were made with a glass electrode and a reference electrode with liquid junction. The method of measurement was based on the experimental design given by Zirino (1975) for shipboard determinations. The pH's measured at 25°C have been corrected to in situ values by using Table VI.3 in Strickland and Parsons (1972). Figure 8 shows the in situ pH as a function of depth, and the station locations are marked on Figure 1. As can be seen, the pH of the deeper water is at about 7.7, while the pH of the surface water (above 30 m) is slightly higher at about 7.9. In seasons where biological productivity is higher, some CO_2 will be removed from the water, and it is anticipated that the pH could rise to about 8.3, at least in the surface waters. The temperature of the deep water varies between 8° and 9°C, while surface waters drop to as low as 5°C in winter and rise to 15°C in summer (Crean and Ages, 1968). The inset area in Figure 7 shows the region normally expected in unpolluted water. For sufficiently dilute chlorine the OCl^-_t form will dominate with the $\frac{OCl^-_t}{HOCl}$ ratio varying from 3 to 10. The higher value is to be expected in surface waters particularly when the pH is higher. This is of some importance since evidence shows that the non-ionized form is more toxic to bacteria (Fair et al, 1968) and also more reactive in the formation of toxic secondary products (Morris, 1967 and Farkas et al, 1949).

There is, however, another factor which should be considered. The addition of chlorine to seawater will cause a pH change according to Equation 3 and Equation 4 since each mole of chlorine produces initially one mole of HCl, and further ionization of hypochlorous acid can potentially liberate a second proton.

Consideration simultaneously of both Equation 3 and 4 allows the equilibrium concentration of the chlorine species to be calculated as a function of pH. The ratio of each species to the total chlorine present is shown in Figure 9 where

$$\alpha_0 = \frac{[Cl_2]}{[Cl_2] + [HClO] + [ClO^-_t]} \qquad (7)$$

$$\alpha_1 = \frac{[HClO]}{[Cl_2] + [HClO] + [ClO^-_t]} \qquad (8)$$

$$\alpha_2 = \frac{[ClO^-_t]}{[Cl_2] + [HClO] + [ClO^-_t]} \qquad (9)$$

Consideration has been taken of the chloride concentration in seawater, which tends to shift Equation 3 to the left on going from fresh water to seawater. From Figure 9 it is important to note that ClO^-_t comprises 10% or more of the chlorine species in seawater only when the pH is greater than 6. From pH 4 to 6 the HClO form is most important, while 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 in Equation 10.

$$HOCl \rightarrow HCl + \tfrac{1}{2} O_2 \qquad (10)$$

(There is of course a chloride generated by this reaction). When some of the chlorine has been lost by this route, it will appear as if a strong acid, HCl, has been added along with the remaining chlorine.

The Effect of Chlorine on Alkalinity and pH

According to Equation 3, the addition of chlorine to seawater can be considered as a titration of seawater with a strong acid. Hydrogen ions can also be added through the secondary ionization of HOCl. (This secondary reaction will not affect the titration alkalinity since for each mole of protons added, one mole of the conjugate base OCl^- is also added. Titration to a pH 4 endpoint will cause all of the OCl^- to be converted back to HOCl. As mentioned above, oxidation reactions removing the OCl^- form (Equation 10) will lower the alkalinity). There may also be a further titrational effect dependant on the pH of the end point since some chlorine will be formed at lower pH's. Reference to Figure 9 will illustrate this clearly.

In the long term, once all of the active chlorine species have been reduced to chloride, two moles of H^+ will have been generated for each mole of Cl_2 added to the seawater. Consider the tank cars which contain a total of 376 metric tons of chlorine. If we accept an alkalinity change of 2% as being relatively insignificant, simple calculations show that dilution with $2 \times 10^8 m^3$ of seawater are required.

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 2.2×10^{-3} mol/l and a pH of 7.9. Using the apparent dissociation constants for the CO_2 system (Horne, 1968) and Kw taken from Culberson and Pytkowictz (1973) for 8°C and 35°/₀₀ salinity, it is possible to calculate what additions of strong acid are required to cause the pH to change to any specified value in a closed system (i.e., CO_2 is not allowed to escape to an atmosphere). Figure 10 shows the titration curve calculated for $C_T = 2.2 \times 10^{-3}$ mol/l. Keeping the initial pH at 7.9 and allowing effect shown in Figure 10.

Titration with chlorine has some similarities to titration with a strong acid, but cognizance must be taken of both Equation 3 and 4. Using the appropriate equilibrium constants of Sugam and Helz (1976), and White (1972), the titration curve has been calculated and is shown on Figure 9 along with the speciation curves. 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 7.4 when $[OCl_t^-] = [HOCl]$. 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 Cl_2 becomes an important species, since the equilibrium of Equation 3 is shifted to the left. Addition of large amounts of chlorine here do not have a great influence on pH. This is particularly dramatic since the <u>logarithm</u> of chlorine added is plotted as the ordinate.

The measured pH values in Malaspina Straits are fairly uniform with depth (Fig. 8) indicating that at least at these two stations at the time of sampling no anomalous behaviour atributable to chlorine was determined.

Effect of Chlorine on Redox Potential

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

$$pE = -\log\{e\} = \frac{F}{2.3}\frac{Eh}{RT} = \frac{Eh}{.059} \qquad (11)$$

where F is the Faraday, R the gas constant (8.31 joules/°Cmole and T the absolute temperature. The redox potential is normally discussed in terms of both pE and Eh, the interrelation being demonstrated in Equation 11.

For oxic seawater the measured pE is found to be approximately 8.5 suggesting that pE is controlled by the O_2/H_2O_2 couple (Breck, 1975).

The addition of chlorine to seawater would be expected to upset this precariously poised system, chlorine being a strong oxidant. If it is assumed that the seawater system becomes controlled by the Cl_2/Cl^- couple then

$$\tfrac{1}{2}\,Cl_2 + e \rightarrow Cl^- \quad E° = 1.3595 \text{ (Horne, 1968)} \qquad (12)$$

From fundamental thermodynamics

$$\Delta G^\circ = -nFE^\circ = -RT\ 2.3 \log K \tag{13}$$

where ΔG° is the standard free energy change and K is the equilibrium constant associated with the respective reaction.

For Equation 12, $\Delta G^\circ = -13.12$ KJ/mol

$$\log K = 23.02 \tag{14}$$

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

For seawater of 35°/oo salinity

$$\{Cl^-\} = [Cl^-]\ _{Cl^-} = 0.55 \text{ x } .66 = .36 \tag{16}$$

($_{Cl^-}$ was taken from Whitfield, 1976)

$$23.02 = -.044 + pE - \tfrac{1}{2}\log P_{Cl_2} \tag{17}$$

$$pE = 23.46 + \tfrac{1}{2}\log P_{Cl_2} \tag{18}$$

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 sufficiently accurate when the couple in Equation 12 controls the redox potential. This indicates in more precise terms what we already intuitively suspected; that chlorine is strongly oxidizing. Reversing the procedure, it obtains directly from Equation 18 that normal oxic seawater with a pE of 8.5 has a negligibly small P_{Cl_2} since $\log P_{Cl_2} \simeq -30$.

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

$$ClO^- + H_2O + 2e \rightarrow 2OH^- + Cl^- \tag{19}$$

$$E^\circ = 0.89 \text{ (Horne, 1968)}$$

$$\Delta G^\circ = -171.5 = -RT\ 2.3 \log K \tag{20}$$

$$\log K = 20.14 = 2\log\{\text{OH}^-\} + \log\{\text{Cl}^-\} + 2\text{pE} - \log\{\text{H}_2\text{O}\} - \log\{\text{ClO}^-\} \quad (21)$$

$$= 2[\log K_w^{Sw} + \text{pH}] + \log\{\text{Cl}^-\} + 2\text{pE} - \log\{\text{H}_2\text{O}\} - \log\{\text{ClO}^-\} \quad (22)$$

$$= 26.40 + 2\text{pH} - 0.44 + 2\text{pE} + .008 - \log\{\text{ClO}^-\} \quad (23)$$

(K_w^{Sw} has been taken from Culberson and Pytkowicz (1973), for a temperature of 25°C and salinity of $35^\circ/_{oo}$. The activity of water in seawater has been estimated from the vapour pressure lowering of $35^\circ/_{oo}$ seawater, Sverdrup et al, 1942).

Therefore

$$\text{pE} = 28.49 - \text{pH} + \tfrac{1}{2}\log\{\text{ClO}^-\} \quad (24)$$

Using the approximation given by Sugam and Helz (1976), for the activity coefficient of the hypochlorite ion in seawater

$$\text{OCl}^- = 0.64 = {}^{\pm}\text{KCl} \quad (25)$$

$$\text{pE} = 28.39 - \text{pH} + \tfrac{1}{2}\log[\text{ClO}_t^-] \quad (26)$$

Equation 26 is simply a different formulation of Equation 18, but it is easier to see the influence of chlorine on pE because by reference to the titration curve in Figure 9 it is now possible to estimate pH.

Use of Equation 5 and 6 along with the estimated value for pH yields pE as a function of chlorine added. This curve is shown in the top part of Figure 9 where it can be seen that pE does not vary greatly over a wide range of total chlorine concentrations. This curve was generated by assuming that no chlorine was removed through oxidation reactions. As indicated earlier, oxidation processes will remove chlorine, but will not remove the HCl generated and therefore a variety of time-concentration paths are possible along the pH and pE curves. These paths will be more or less independent depending on how much oxidizable material there is in seawater.

Equation 18 and 26 are also useful in determining the oxidation state of the elements or compounds 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.

Kinetics

There is general agreement that the adsorption of chlorine by water (Equation 3) is extremely fast (Shilov and Solodushenkov, 1936, Morris and Carrell, 1946, Spalding, 1962). In fact, Shilov and Solodushenkov (1936) found the reaction to be almost complete in less than one second at 1°C, a temperature somewhat lower than any expected in Georgia Strait waters. Spalding (1962) considered two possible reactions

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^- \qquad (3)$$

$$Cl_2 + OH^- \rightarrow HOCl + Cl^- \qquad (27)$$

His results indicated that between pH 3 and 10.5 the first equation applied, and considering a copious quantity of water is available, Equation 3 can be kinetically treated as a first order equation. Spalding measured a first order rate constant of 20.9/sec at 25°C with an activation energy of 62.8 KJ/mol. The half life of the reaction at 8°C can be calculated at about .1 sec, and therefore conversion of Cl_2 to HOCl is very rapid.

The production of chlorine hydrate ($Cl_2 \cdot 6.2\ H_2O$) appears to be transport controlled with the slowest step occurring at the chlorine-water interface (de Graauw and Rutten, 1970). Therefore, agitation or turbulence will encourage the production of the hydrate.

The Chlorine Demand of Seawater

So far we have considered the various equilibrium reactions of chlorine in water assuming that no removal mechanism were operating. This, of course, is not the case in nature and a variety of removal paths are available. Given sufficient time and mixing, all of the chlorine with a +1 valance will eventually be removed through redox reactions. A variety of compounds naturally present in seawater will be important in the removal of chlorine, some of which are listed below (White, 1972).

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 short term chlorine interaction are those containing nitrogen (1, 2, 3 and 5 of the above list), especially ammonia. The reaction of chlorine and ammonia in dilute solutions leads to the formation of the chloramines.

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \qquad (28)$$

monochloramine

$$HOCl + NH_2Cl \rightarrow HHCl_2 + H_2O \qquad (29)$$

dichloramine

$$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O. \qquad (30)$$

nitrogen trichloride
(trichloramine)

The above reactions are not redox reactions in that chlorine still maintains its +1 valance and these compounds still have oxidizing, disinfecting and biocidal capacity. An excellent and very complete review of the interaction of chlorine with ammonia and also other compounds is given by White (1972), to which the reader is referred for more detail than is provided here. Jolley (1973) has also collected together 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 as hypochlorous acid is termed "free available chlorine residual" or "free residual" (ASTM Standards, 1976). 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 chlorine quickly from the water. Loss of chlorine in this manner is referred to as the "chlorine demand" of the water (Singley, 1973). Chlorine demand, then, is that amount of chlorine which the water can remove by reducing the Cl^{+1}, to Cl^{-1} or irretrievably tying up the chlorine in some organic compound. Operationally, demand is defined as the "difference between the amount of chlorine applied to a treated supply, and the amount of free combined or total available chlorine remaining at the end of a contact period" (APHA, 1971).

With respect to chlorination, seawater has one important difference from fresh water. It contains an appreciable quantity of bromide, with 67.3 mg/Kg in seawater of 35°/₀₀ salinity (Wilson, 1975). As mentioned while discussing the effect of chlorine on the pE of seawater, it is thermodynamically possible for chlorine to displace the bromide in seawater with a loss of about 30 mg/Kg of chlorine, and a production of about 67.3 mg/Kg bromine in 35°/₀₀ seawater. Bromine is then free to react in an analogous manner to chlorine producing hypobromous acid and the bromamines. Most instrumental methods do not differentiate bromine and chlorine contributions, and therefore seawater measurements have commonly been referred to in terms of the chlorine demand. A method which reportedly could differentiate between chloramines and bromamines was devised by Johannesson (1958), but Duursma and Parsi (1976) could not obtain satisfactory results in their laboratory. In the remainder of this report we shall refer to all measurements in terms of chlorine, tacitly realizing that some bromine or brominated species will be contributing.

Griffin (1944) 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 suddenly 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 M.V. Pandora II during an Ocean Chemistry cruise 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 (1976) and the Fischer and Porter Instruction bulletin for the amperometric titrator made by that company. The reader is referred to these for details of the method. The Fischer and Porter Model 1771010 Amperometric Titrator was used for all chlorine determinations, and does not distinguish between chlorine and bromine contributions.) Figure 11 shows the essential features of this breakpoint curve and several aspects should especially be considered. The curve does not pass through the origin due to some initial chlorine demand caused by some species in seawater which are readily oxidized within the half hour chlorination period. The first part of the curve lies in the region where most of the chlorine is tied up as monochloramine. After the maximum, dichloramine may be formed, an important compound since it participates in further reactions which lead to the eventual oxidation of ammonia by deamination. The downward slope in Figure 11 results in a measured increase in chlorine demand. The minimum is the breakpoint beyond which free chlorine residual exists. In fresh water there is also a small portion of dichloramine and trichloramine present. Duursma and Parsi (1976) in some very recent investigations measured the interaction of ammonia and chlorine in seawater with relatively high doses of both chlorine and ammonia (up to 710 mg/Kg Cl_2). Their experiments point out some fundamental differences between the formation of chloramines in seawater and in 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 the dichloramine does not persist in detectable quantities. Oxidation of ammonia via the chloramines can result in various possible nitrogen species including N_2, NO_3^-, N_2O, and NO (White, 1972).

While investigating the chlorine demand of water as a function of time, Taras (1953, 1950) found that chlorine demand could be expressed by the equation

$$D = kt^n \qquad (31)$$

where D is 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 as such helps to define which species are responsible for the chlorine demand observed. The higher the exponent, the slower the reaction, and also the more complicated the reacting species.

Some experiments were made on the chlorine demand of seawater as a function of time on samples obtained in August 1976 from Saanich Inlet in the vicinity of the small CEPEX enclosures. Both a 2 meter and a 30 meter sample are shown in Figure 12 (each seawater sample was chlorinated with 5 mg/l chlorine initially). The first chlorine demand measurement appears to be low possibly due to experimental error or perhaps due to an induction period peculiar to the seawater system. (The 2 m sample also had the first point somewhat lower than might be expected.) The exponent of t was found to be .22 for the 30 m sample and .20 for the 2 m sample, indicating that compounds other than ammonia are also responsible for some of the chlorine demand. Water with the nitrogen component mainly due to ammonia have exponents in the .01-.08 range (White, 1972). A Taras plot (Fig. 13) was also made for a sample of surface sediment obtained in Georgia Strait several miles off Point Grey. In this case 5.2 grams of sediment (wet weight) were placed in 5 litres of demand-free water which was then chlorinated to 5 mg/l. The sample was continuously stirred by a magnetic stirrer with a Teflon stirring bar throughout the measurements. Figure 12 shows that again, the early measurement was depressed, while the exponent of t calculated from the later points was .28 indicating the likely occurrence of more complicated nitrogenous compounds than ammonia. The 5 g sample also had a fairly high demand removing all of the chlorine in the 5 litre flask within four hours. (All demand experiments were run under ambient laboratory light conditions.)

These experiments show that seawater may be expected to have a short term demand of about 1.5 mg/l (Fig. 11). Sediment appears to have a fairly high demand with 1 g (wet weight) of surficial mud capable of quickly removing 2 mg of chlorine from a 1 litre volume. This agrees well with the estimate given by White (1972) 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. Examination of Figure 12 shows that after two days only 3 mg/l chlorine had been removed from the 30 m seawater sample. The same was true for the 2 m sample.

Duursma and Parsi (1976) investigated the persistance of chlorine in seawater using far higher concentrations of chlorine than used in our studies, with chlorine doses of over 1600 mg/l. They found that under these circumstances a more or less rapid loss of chlorine was often seen with the higher dose during the first few minutes. Aeration augmented this effect causing a seawater solution initially dosed with 1400 mg/l of chlorine to fall to about 1100 mg/l after ten hours. They hypothesized that some of the chlorine may have been removed by gas bubbling, an unlikely mechanism since at the pH of their chlorinated seawater (greater than 10) the amount of free chlorine is very low (see Fig. 9). There does not at present appear to be any reasonable explanation for this behaviour, and their investigations at lower doses of chlorine (below 600 mg/l) do not show this loss.

A possible direct removal of chlorine from seawater is possible by a light stimulated reaction

$$Cl_2 + H_2O \rightarrow 2HCl + \tfrac{1}{2}O_2 \qquad (32)$$

Duursma and Parsi (1976) studied the effect of light on persistence of chlorine in seawater with chlorine concentrations below 35 mg/l. The found no significant difference in chlorine behaviour between the light and dark conditions, and suggest that formation of bromine may be responsible since the bromine reaction analogous to Equation 32 was not photochemically mediated under the experimental conditions.

Gaseous Explosion

When a liquified gas is spilled onto or injected into a second fluid, there is a possibility of forming superheated liquid drops. In this case, the temperature of the drop is elevated above its normal boiling point.

Under the usual circumstances when a liquid exposed to a gas phase (the atmosphere) is raised to its boiling point it will simply boil and maintain 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 adsorb gas and present a gas-liquid interface where a bubble can be formed. Even this process is sometimes not sufficient to prevent superheating, and most chemists are familiar with the phenomenon of "bumping" while attempting a distillation. The use of boiling chips with rough porous surfaces can prevent this by introducing a large gas-liquid interface. Kinetic analysis shows that the probable formation of a bubble within a liquid (homogeneously) at the normal boiling temperature is very low. Small bubbles tend to collapse before they reach a critical size where surface tension effects are not so important.

In the case where an immiscible drop of liquified 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 reproduceably heat n pentane to 146-147°C at atmospheric pressure (Reid, 1976). 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 a superheated liquid can explode with violence.

Since the boiling point of chlorine is -34.5°C at atmospheric pressure, and the temperature of seawater in Georgia Strait may be expected in the 5-15°C temperature range, the injection of liquid chlorine into the water will result in the formation of superheated drops. It is important to ascertain the liklihood of an explosion or explosions following rupture of the tank cars. This discussion applies only to that part of the water column where chlorine gas is thermodynamically stable. At depths where chlorine would normally remain a liquid, gaseous explosion will never be a problem.

Thermodynamic stability analysis shows that for a pure liquid the superheat limit occurs when (Beegle et al., 1974)

$$(\frac{\partial P}{\partial V})_T = 0 \quad . \qquad (33)$$

Using this thermodynamic criterion and the Redlich-Kwong (1949) equation of state, Reid (1976) has provided a generalized curve of reduced pressure (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 temperatures respectively This curve gives a very adequate representation of experimental observations on many gases.

Based on this curve and the critical pressure (76.8 bars) and critical temperature (144°C) of chlorine, the water temperature would have to be in excess of 100°C before explosion could take place at atmospheric pressure. Clearly, this rules out gaseous explosion as a result of mixing chlorine with Georgia Strait water.

Chlorine Release in Seawater

On August 20, 1976, some small-scale chlorine release experiments were performed in Saanich Inlet at a series of depths from 25 m to 145 m. A small size cylinder (10 cm diameter x 36 cm length, Canadian Liquid Air) was half filled with liquid chlorine and padded to 35 bars pressure with nitrogen. The outlet was connected through a short length (1 meter) of .3 cm OD stainless steel tubing, acting as a flow restrictor, to a Whitey ball valve. After the ball valve, a short piece of .6 cm stainless steel tubing was connected with a one way check valve at the end, and a short piece of .6 cm OD Teflon was connected last. The ball valve was opened and closed outside the Pisces by a Whitey 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. Figure 14 gives a schematic diagram of the equipment, and Figure 15 shows how the system was arranged on the outside of the Pisces.

During the release experiments visual examination, colour 35 mm slides and super 8 movies were used to document the behaviour of chlorine at various depths when released into the water. In the following description it will be assumed that every 10 meters depth of seawater is approximately equivalent to 1 bar of pressure so that, for example, 80 meters would have a total pressure 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 (Saunders and Fofonoff, 1976).

Initially on the dive, the Pisces descended to the bottom of Saanich Inlet about 190 m. Although the order for the cylinder specified padding the void space with 35 bars (500 psi) of N_2, chlorine did not come out at this depth. It is possible that the cylinder was not padded to sufficient pressure or, more likely, some of the N_2 dissolved in the chlorine causing a reduction in pressure according to Henry's law. The first chlorine emerged at 145 m (15.7 bars) as green liquid drops, some running down the tube as a thick syrup-like fluid and some squirting out and then quickly descending in drops about 1/2 cm in diameter (Fig. 16). No hydrate was seen although the chlorine rapidly disappeared from sight below the Pisces windows before mixing to any degree with the water. As suggested in the section on kinetics, the hydrate formation process is transport controlled at the chlorine-water interface and slow mixing here probably slowed down hydrate formation even though the hydrate is thermodynamically stable (Fig. 5).

At 90 meters the chlorine emerged more vigorously (due to reduced hydrostatic pressure) and could be observed for a longer time period than before. Figure 17 shows the green liquid coming up out of the tube, and then rapidly descending. Some yellowish hydrate could be seen forming on a few of the liquid chlorine drops, and fine white flakes of hydrate were clearly seen, dispersed through the water a short time after the chlorine had 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/cc which indicates that it could eventually sink at a rate dependent on particle size. Figure 17, also taken at 90 m, shows more clearly the liquid chlorine-hydrate clumps which formed shortly after injection into the water. These clumps slowly sunk below the Pisces windows.

At 60 meters depth the chlorine shot out in a fairly dispersed plume and formed hydrate more readily than at 90 meters probably due to turbulent mixing, and a finer dispersion of chlorine into small drops. Figure 19 shows the chlorine plume, and some of the liquid drops with hydrate attached are visible to the right of the tube and level with it. Some small bubbles were also seen, but these were probably due to N_2 being released from the chlorine similar to the release of CO_2 on opening a carbonated drink.

At 45 meters a similar behaviour was observed but the liquid chlorine-hydrate clumps which formed initially had occluded or attached bubbles which caused them to rise quite rapidly. At this depth, liquid chlorine, hydrate and gaseous chlorine were all seen although the gaseous chlorine formed slowly. Fine flakes of hydrate were seen shortly after chlorine injection as shown in Figure 20.

At 25 meters no liquid was observed at all, and the chlorine came out as a steady gas plume (Fig. 21). Outgassing and expansion of dissolved N_2 may have contributed to this, but the general colour showed that a large portion of the gas was chlorine. Since liquid chlorine still remained in the cylinder (which was inverted) at the end of the experiment, the gas seen at this level was generated from liquid chlorine, and not from gas coming directly from the cylinder. No hydrate was seen in the water near the injection point, but it could possibly have formed further up in the water column as the gas plume rose. How far the gas bubbles rose was impossible to tell from inside the Pisces Some gas was sighted near the surface, but only when the Pisces had cleared its ballast tanks. There was no direct evidence of chlorine at the surface. In accordance with the theory given in the section on gaseous explosion, no violent explosions were seen at any point in the water column during the chlorine releases.

Some experiments on chlorine-seawater interaction were performed by Macmillan-Bloedel (R.W. Cunnington, 1975) in which chlorine was released into seawater in the laboratory, and into the surface water in Burrard Inlet. They used a 25 litre chlorine cylinder inverted, so that only liquid chlorine was released (The tank was not pressurized with air or N_2.) Gaseous chlorine and the hydrate formed during all of the experiments, some of the gas apparently reaching the surface from a depth of 20-30 cm. Much of the chlorine was tied up in "golf ball"sized lumps of hydrate which came to the surface and dissociated into the aqueous phase within a couple of minutes. (The surface temperature of the water was probably less than 10°C.)

The physical behaviour of chlorine in seawater conforms quite closely with thermodynamic prediction (Fig. 2-5). Gas forms above 45 meters and the hydrate clumps rise due to attached bubbles above the depth. In the event of a large spill of chlorine at less than 45 meters, it is impossible to give an exact estimate of the behaviour, but the majority of chlorine should be tied up as a hydrate before reaching the surface. At very shallow depths, some chlorine gas could break the surface and escape to the atmosphere, but how much would escape depends directly on the magnitude of the leak, the depth of the water and the temperature. Lumps of hydrate buoyed by occluded gas could also float to the surface, but would tend to dissolve into the water rather than release chlorine to the atmosphere.

Chlorine Release in the Atmosphere

During an Ocean Chemistry Cruise on the CSS Vector we had the opportunity of observing first hand an accidental release of a mixture and hydrochloric acid from FMC Co. at Squamish on November 29, 1976. The Vector, which at the time of release was on station about 500 meters off shore directly in front of FMC was forced off station for about two hours while the chlorine dispersed. It was estimated that a mixture consisting of 76 kg of chlorine and 4.5 kg of hydrochloric acid was lost during the discharge. The amount of chlorine lost corresponds to less than 0.1% of that contained in one of the tank cars. Winds at the time were light (about 3 knots) and from the west. Initially, a yellowish-white cloud was seen at the FMC site (Fig. 22) but soon it spread across the water toward Darrell Bay as an elongated whitish mist (Fig. 23). The whitish mist, or remants of it were visible along the eastern side of Howe Sound for over three hours after the release (Fig. 24), and on returning to station after two and a half hours there was still a strong chlorine smell in the air. Since the chlorine which was released was mixed with some hydrochloric acid, the whitish mist was most likely caused by the interaction of HCl with water vapour in the air. Pure chlorine when released might not be so visible, although water vapour could lead to the production of HCl by way of Equation 3.

Two researchers on a field trip were conducting a sampling program throughout the night (November 29-30) on the tidal flats in front of FMC. They both detected chlorine in the air at times, and reported that on occasions it smelled strongly while at other times they did not notice it depending on the wind direction. Both developed sore throats as a result of the exposure (Thomas and Erickson, 1976).

Toxicity (Marine Environment)

As has been shown in the previous sections, the chemistry of chlorine in seawater can be fairly complex, and prediction of reaction products in the natural environment is virtually impossible (Mattice and Zittel, 1976). In spite of this, it appears that toxicity can be fairly well predicted provided the correct type of information is available.

After water has been chlorinated, only three basic forms of chlorine need be considered for toxic effects.

1. Free residual chlorine existing as either $HOCl$, OCl^- or even as free Cl_2. The equilibrium between these three species has already been dealt with in some detail, and it suffices here to repeat that the system is very pH dependent (Fig. 9).

2. Combined residual chlorine, specifically the chloramines but also compounds formed with more complex nitrogenous substances such as proteins and amino acids.

3. Apparent chlorine demand chlorine. This category covers that chlorine which has been removed from the system by redox reactions resulting largely in the formation of chlorides. Operationally, it is the difference between the chlorine added, and the "active" chlorine determined by some suitable technique.

Of these three forms the third contributes almost nothing to toxicity in seawater. In the case of polluted waters containing high concentrations of anthropogenic materials some toxic secondary products may be formed, for example cyanogen chloride (Allen, et al., 1946, 1948) chlorophenols (Parker, 1935; Hopkins and Bean, 1966) 5-chlorouracil and 4-chlororesorcinol (Jolley, 1973). These compounds should not be important in open ocean water and it will be considered here that chlorine removed by chlorine demand has been effectively destroyed.

A further consideration peculiar to seawater is the possibility of producing brominated compounds due to the displacement of bromide from the seawater by chlorine. Toxicity studies of chlorine in seawater have traditionally not been concerned about the generation of bromine, but operationally this should not cause problems since toxicity measured as a function of chlorine addition will cover combined effects of chlorine and bromine. The bromide in seawater may indeed explain observed differences in toxicity of chlorinated fresh water and chlorinated seawater. In the remainder of this section reference will be made only to chlorine while it is realized that some or all of the chlorine may be converted to bromine in seawater.

The combined and free residual chlorine cause almost all of the toxic effects in natural waters so that it is important to consider chlorine remaining in both of these two forms after chlorination, rather than the original dose of chlorine added (Merkens, 1958; Doudoroff and Katz, 1950).

Whether the chlorine is in the free or combined form does not seem to matter greatly as far as toxicity is concerned, with both free chlorine and the chloramines exhibiting the same order of magnitude of effects (Brungs, 1973). Evidence has been presented that free chlorine is more toxic (Merkens, 1958; Rosenberger, 1971) and that the chloramines are more toxic (Holland, et al., 1960). The experiments were not strictly comparable, and it is probable that other environmental factors must be considered in determing which form is more toxic. The concentration of total residual chlorine (free and combined) appears to be both necessary and sufficient to determine toxicity (Brungs, 1973; Mattice and Zittel, 1976). (The total residual chlorine is best determined by the amperometric, or ferrous DPD method. The orthotolidene method has been critized as inaccurate by Mattice and Zittel, 1976.)

So far we have mentioned that the total concentration of available chlorine is most important when considering toxic effects. Of equal importance is the time of exposure. Therefore, when talking about toxicity of chlorine, it is most important to consider the dose-time anticipated. Mattice and Zittel (1976) in their recent review have taken all of the literature data and have constructed a most useful dose-time curve for the toxicity of chlorine both in fresh water and in seawater. Acute and chronic toxicity thresholds have been estimated from a statistical analysis of the compiled data, and are shown in Figure 24. The chronic toxicity threshold is the level of chlorine below which no toxic effects result regardless of exposure time. The acute toxicity threshold is constructed from consideration of dose-time effects, where high concentrations can be endured for shorter time periods. There is probably a limit on the acute threshold curve where higher concentrations of chlorine do not shorten death time.

From Figure 24 it can be seen that the chronic toxicity threshold of chlorine in the marine environment is about .02 mg/l. Since the threshold is a statistical creation, we cannot say that there will be no toxic effects from concentrations below this, but we can say that the chance of mortality is very small, and becomes smaller the further below the threshold line the total residual chlorine concentrate is.

Exposure to higher chlorine concentrations can be endured by a wide spectrum of life forms for a short time period with a .1 mg/l level for one minute not contributing too great a hazard.

These toxicity thresholds have been generated by reference to tests on many different animals in a variety of developmental stages. As a result the thresholds tend to represent the safety limit for the most sensitive species, and will in general err on the side of safety.

Toxicity (Atmospheric)

Chlorine is an extremely irritating substance to mucous membranes and the respiratory system. The minimum concentration causing slight irritation is about 1 μl/l (Matheson Gas Data Book, 1966) but chlorine cannot be detected in the atmosphere by smell until it reaches a level of about 3.5 μl/l. The maximum level which can be breathed for one hour without causing damage is 4 μl/l. A detectable odour of chlorine therefore indicates that there is a safety hazard, and steps should be taken to reduce chlorine inhalation. At a level of 15 μl/l there is an immediate throat irritation, and levels of 50 μl/l are dangerous even for short exposures (less than 30 minutes) (Dangerous Properties of Industrial Materials, 1975). Levels of 1000 μl/l are likely to be fatal after a few deep breaths. Chlorine when inhaled reacts with water to form HCl and nascent oxygen both of which attack tissue and can result in pulmonary edema.

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.

2. Chlorine interacts with water on dissolving 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 even toxicity.

3. Chlorine solutions in seawater will be much more strongly oxidizing than normal oxic seawater, and it is likely that the 67.3 mg/l bromide in 35°/₀₀ salinity seawater will be converted to bromine.

4. Most of the chlorine speciation reactions are rapid, and hydrate formation is very fast,being transport controlled. It is, therefore, anticipated that given mixing, most of the chlorine will quickly form hydrate which can then dissolve on further dilution with water. Even if tank car rupture occurs in shallow water, most of the chlorine should be tied up as a hydrate.

5. The chlorine demand of seawater is about 1.5 mg/l (half hour) and about 3 mg/l after two days. Dilution of chlorine to 3 mg/l should result in it being removed via redox processes within a couple of days.

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

7. Gaseous explosion caused by localized superheating of liquid chlorine is not expected to be a problem at the anticipated water temperatures.

8. Chlorine is expected to exhibit toxic effects when present above .02 mg/1, but should not cause problems below that level. Once the chlorine has been removed by the natural demand of seawater it is effectively out of the system. Secondary toxic products should not become a problem in a relatively unpolluted area such as Malaspina Strait. If the tank cars are in deep water, leaked chlorine should settle to the bottom and toxic water formed from mixing the chlorine with seawater should thereafter remain in deep water until sufficient dilution removes the chlorine below toxic levels.

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TABLE I

Conversion of Common Units to SI Units

To Convert From Common Unit	To SI Unit	Multiply By
Atmosphere (Atm)	Bar	1.0133
Calories (Cal)	Joules (j)	4.184
pounds/sq inch (psi)	Bar	.06895
Tons (long)	Metric Tons	1.106

TABLE II

Selected Properties of the Chlorine Water System

Chlorine		
Molecular Weight	70.9 g/mol	
Boiling Point	-34.5°C	1
Specific Gravity (liquid) 0-20°C	1.47-1.41	1
Latent Heat of Vaporization 28.3°C	60.6 cal/g	1
Specific Heat (liquid)	0.226 cal/g	1
Specific Heat Cp (gas)	0.114 cal/g	1
Hydrate		
Composition ($Cl_2 \cdot n\ H_2O$)	n = 6.2	2
Critical Decomposition Temperature	28.3°C	2
Specific Gravity	1.23	3

Heats of Reaction

a) $Cl_2\ (g) + n\ H_2O\ (l) \rightarrow Cl_2 \cdot n\ H_2O$ (Cal/mol at 28.3°C)	16,550	2
b) $Cl_2\ (l) + n\ H_2O\ (l)_{H_2O} \rightarrow Cl_2 \cdot n\ H_2O$ (Cal/mol at 28.3°C)	12,253	2
c) $Cl_2\ (l) + H_2O\ (l) \rightarrow HClO_{ag} + HCl_{ag}$ (Cal/mol at 25°C)	4,420	3

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[1] Matheson Gas Data Book

[2] Fernandez, et al.

[3] CRC Handbook of Chemistry and Physics, 50th edition, 1970.

List of Figures

19. Chlorine plume at 60 meters. Liquid chlorine drops with hydrate attached are visible to the right of the tube above and below the nozzle.

20. Fine flakes of hydrate generated shortly after chlorine release at 45 meters. Flakes similar to these were also seen at 60 meters and 90 meters.

21. Plume of gaseous chlorine at 25 meters.

22. Chlorine "cloud" at Squamish shortly after an accidental discharge from FMC.

23. Elongated chlorine cloud about half an hour after the release.

24. Chlorine mist hanging above the waters of Howe Sound about three hours after the release.

25. Acute and chronic toxicity thresholds for chlorine in seawater.

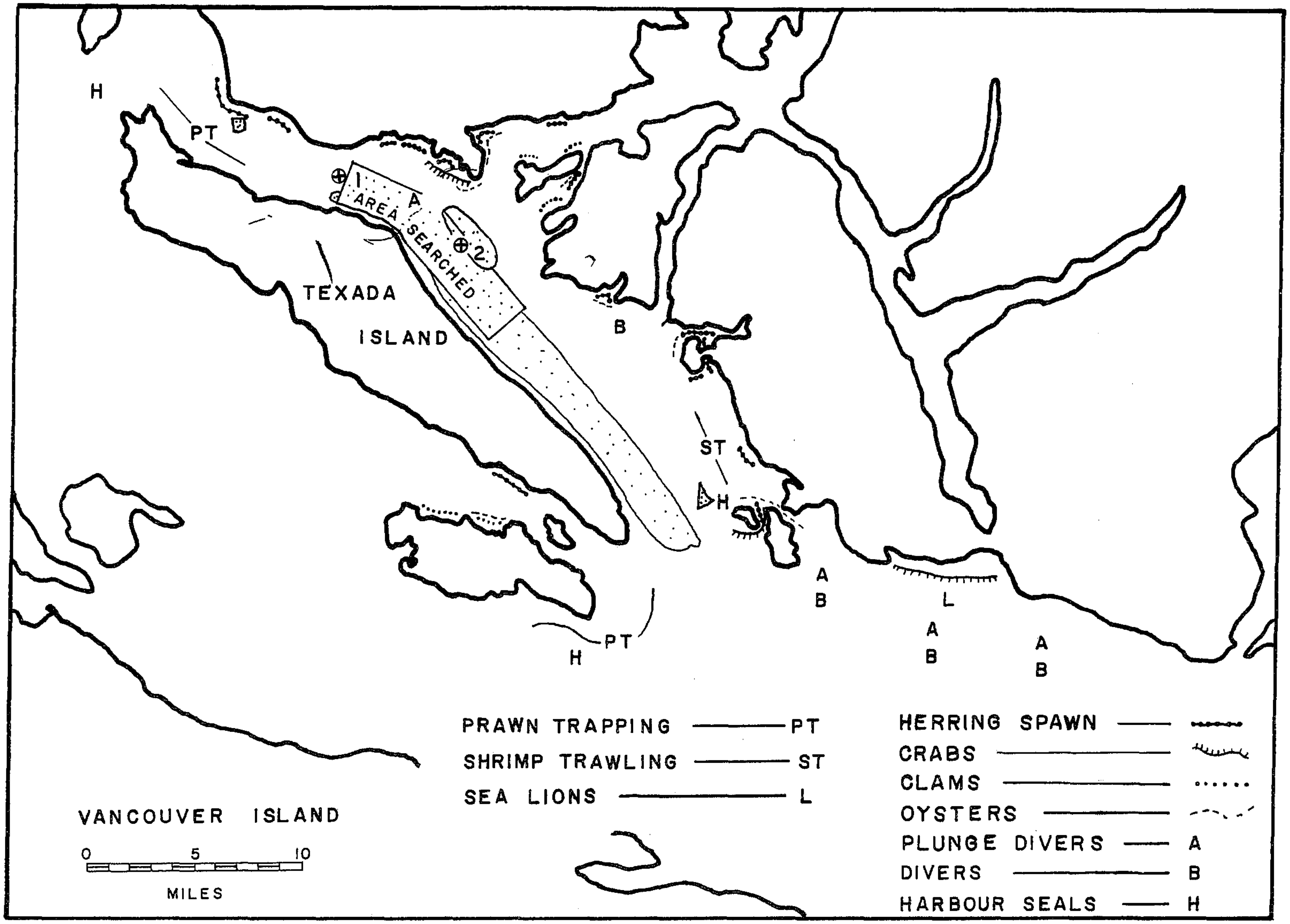

Figure 1. The area where the tank cars are thought to be lost. Included on the chart are the two station locations where pH profiles were determined, vulnerable biological resources, and the areas which have been searched.

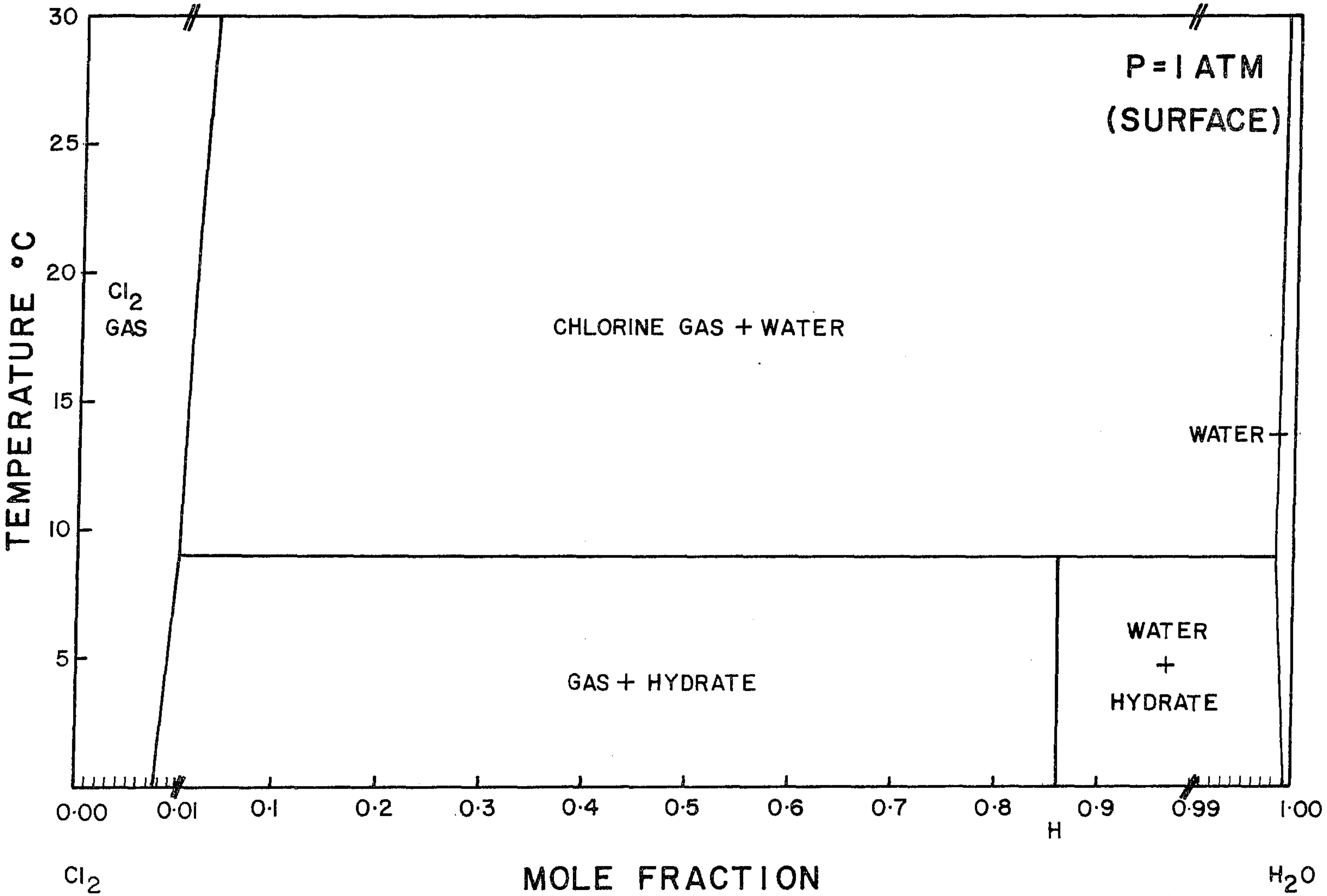

Figure 2. Phase diagram for the chlorine-water system at 1 bar pressure (surface).

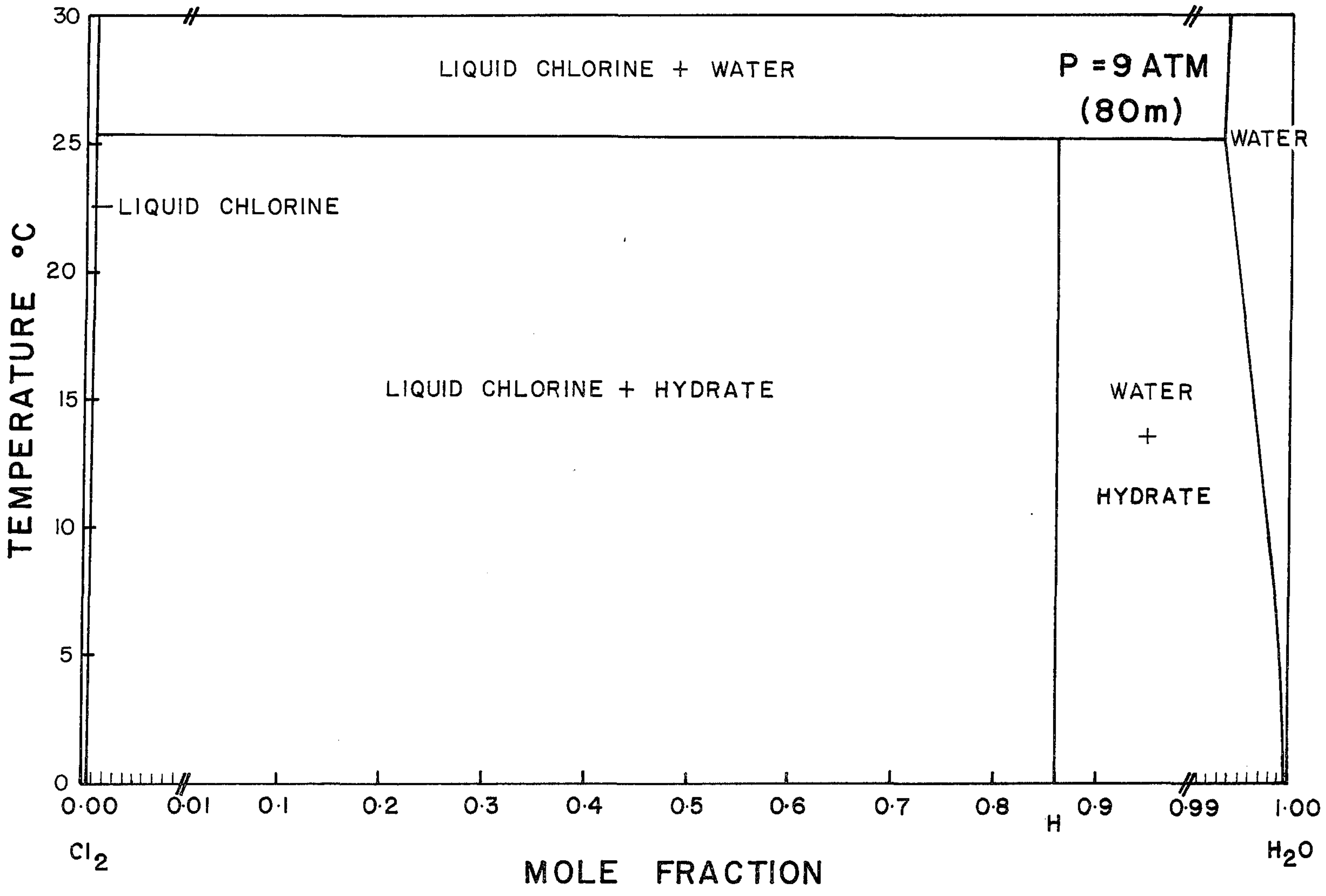

Figure 3. Phase diagram for the chlorine-water system at 9 bars pressure (approximately 80 meters depth).

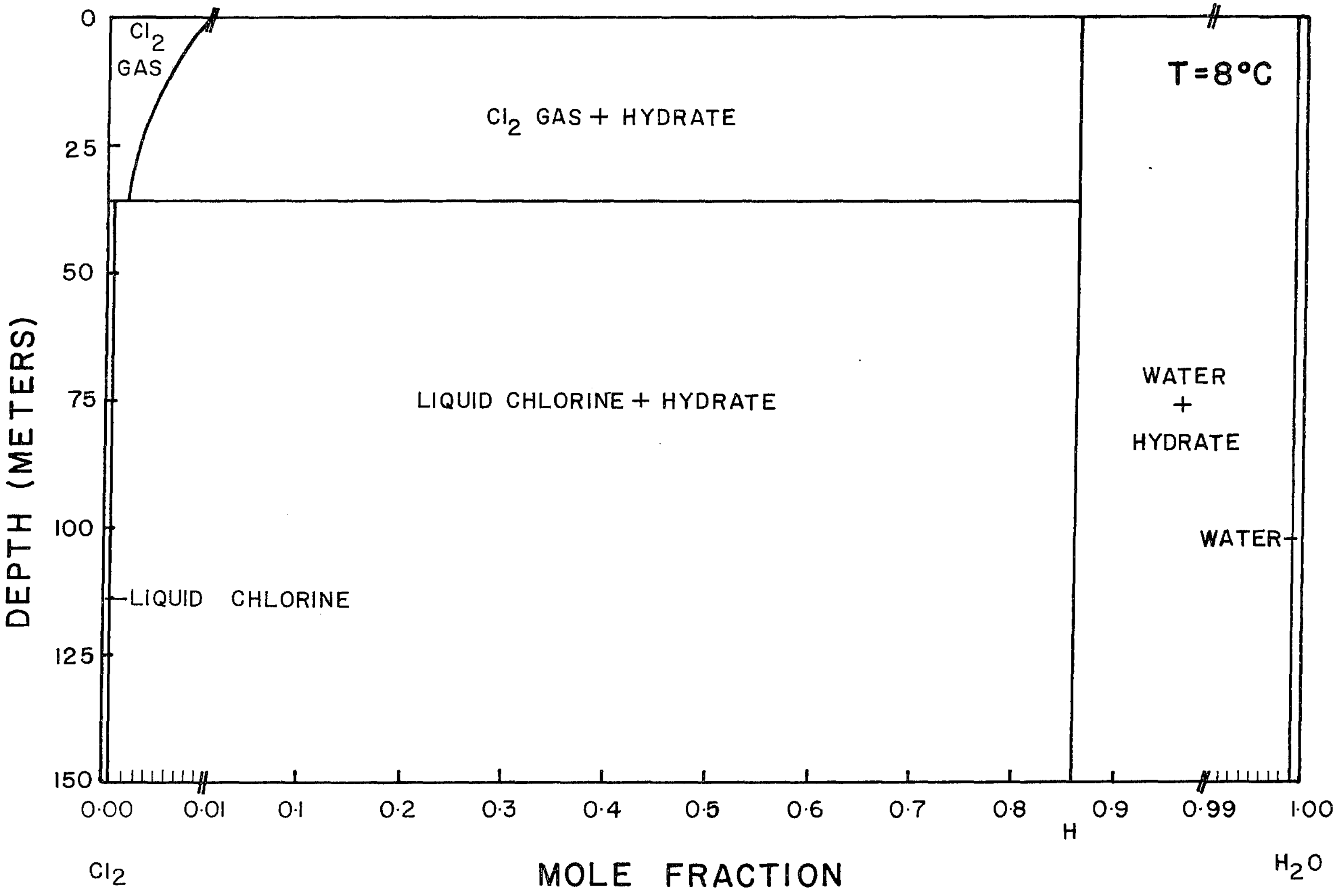

Figure 4. Phase diagram for the chlorine-water system at 8°C.

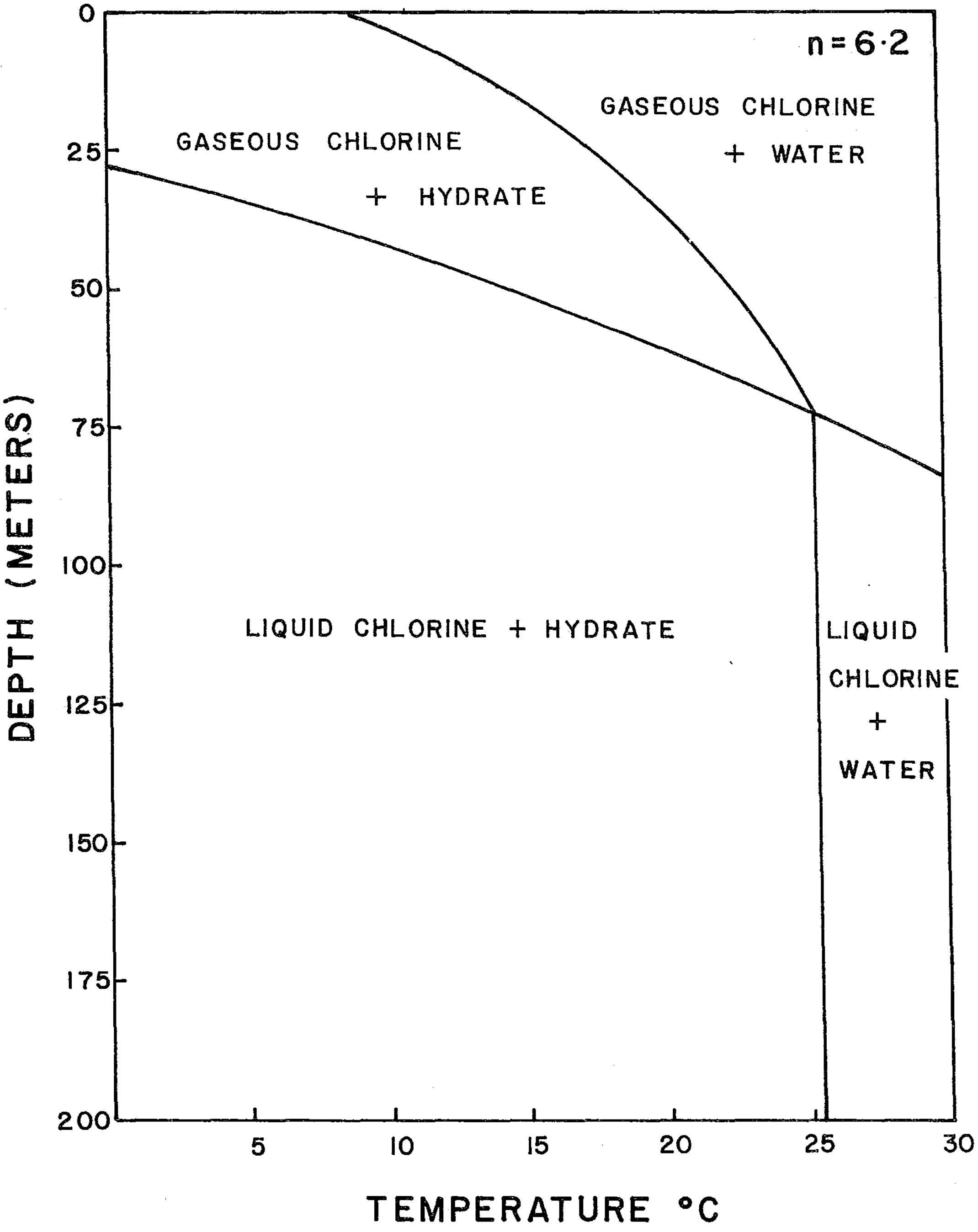

Figure 5. Phase diagram for the chlorine-water system at the hydrate composition.

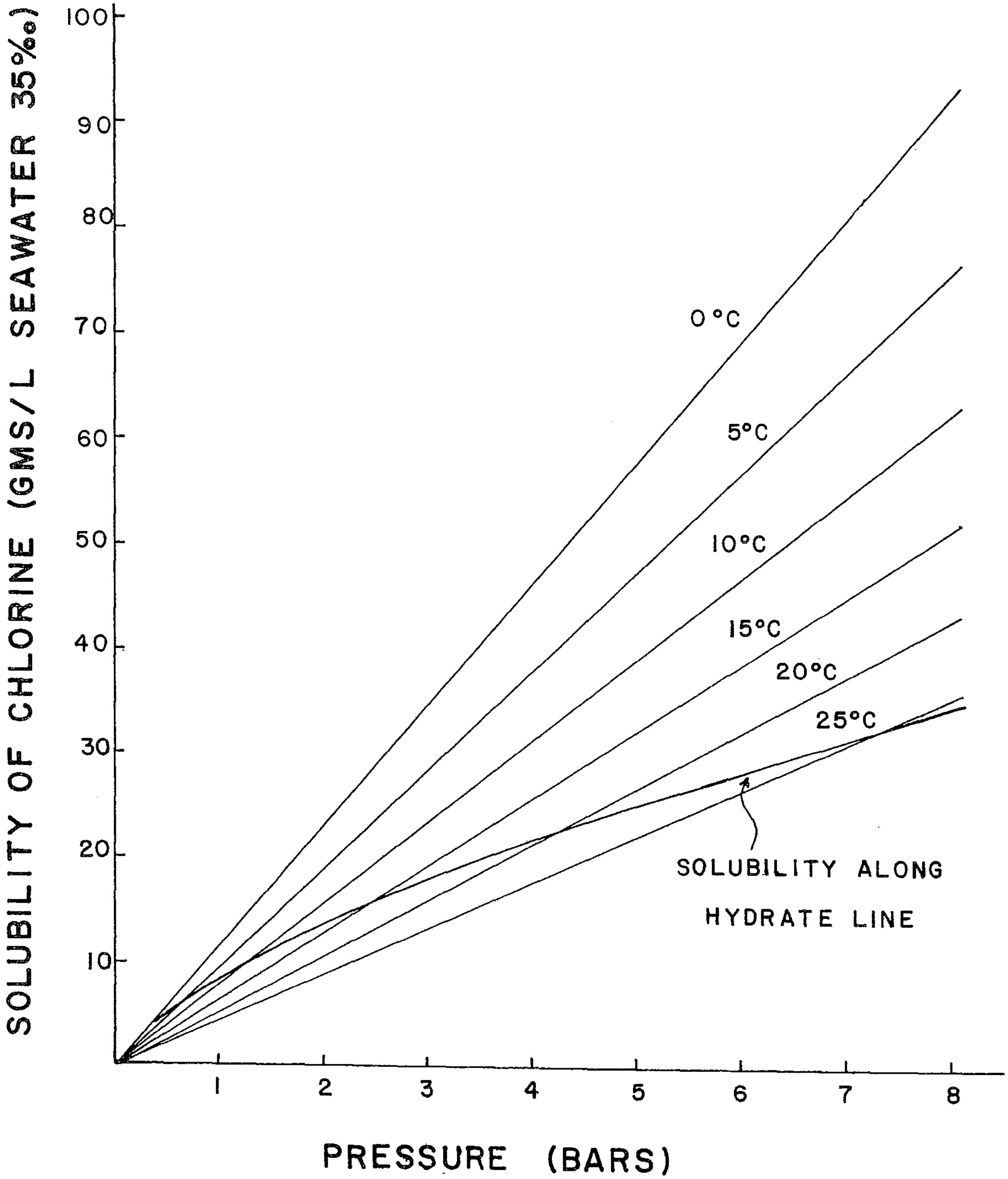

Figure 6. Solubility of chlorine in seawater as a function of pressure and temperature.

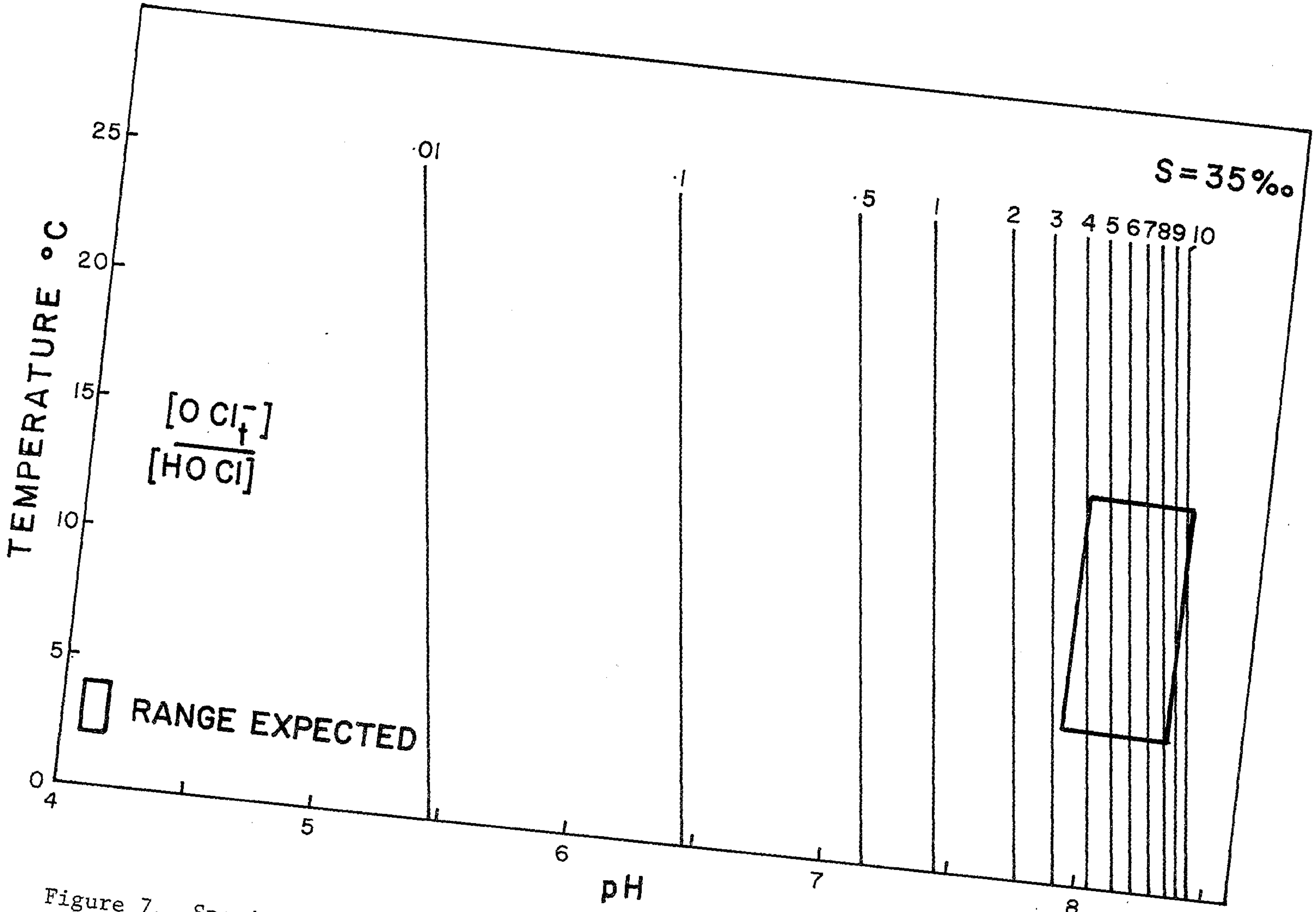

Figure 7. Speciation of hypochlorous acid as a function of pH and temperature.

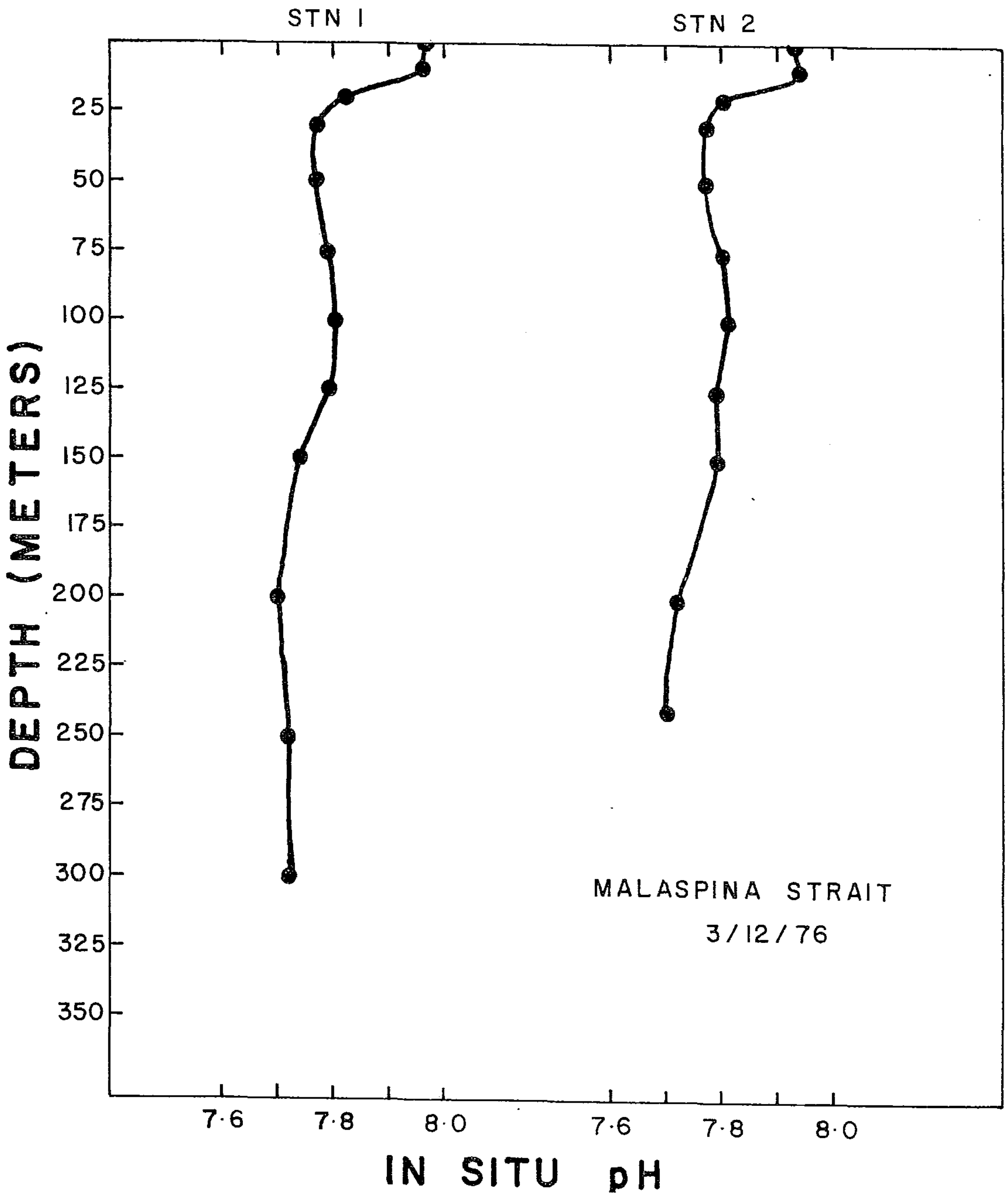

Figure 8. In situ pH measured as a function of depth for two stations in Malaspina Strait (see Fig. 1).

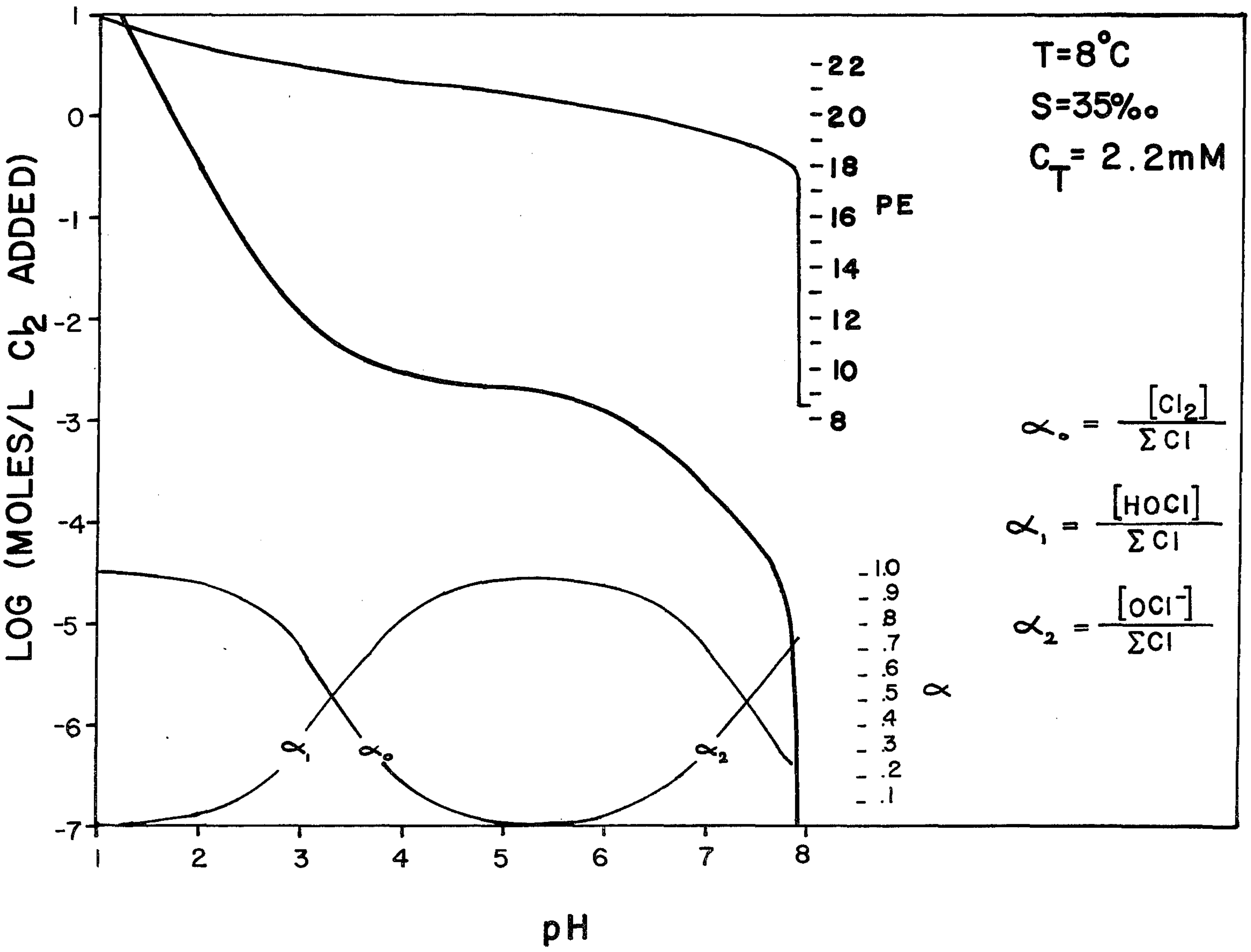

Figure 9. The speciation of chlorine in seawater as a function of pH. Shown also is the titration curve expected when chlorine is added to seawater, and the redox potential as a function of chlorine added.

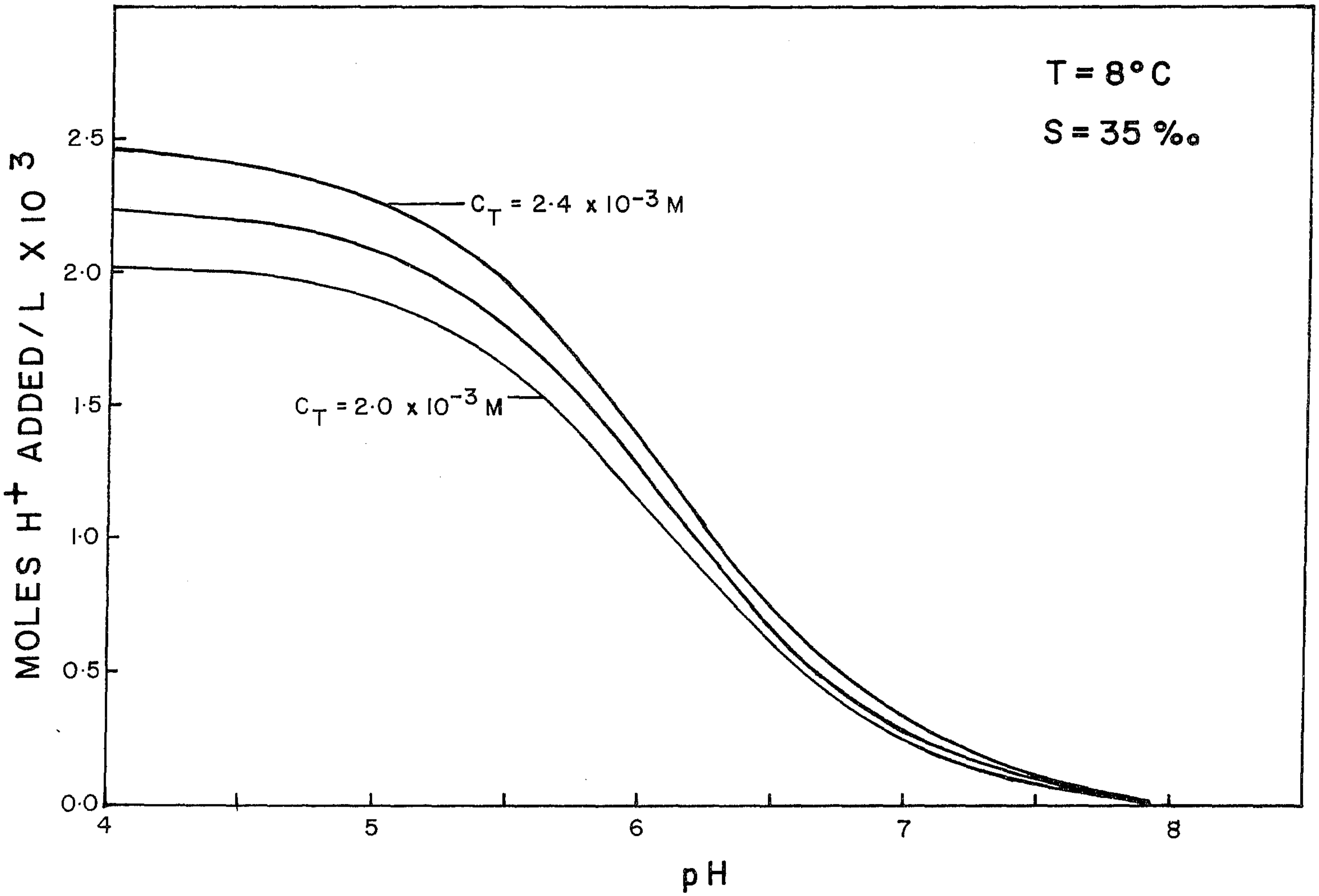

Figure 10. Titration curve for seawater with a strong acid (HCl) for seawater with an initial pH of 7.9, and a total carbonate concentration from 2.0×10^{-3} mol/l to 2.4×10^{-3} mol/l.

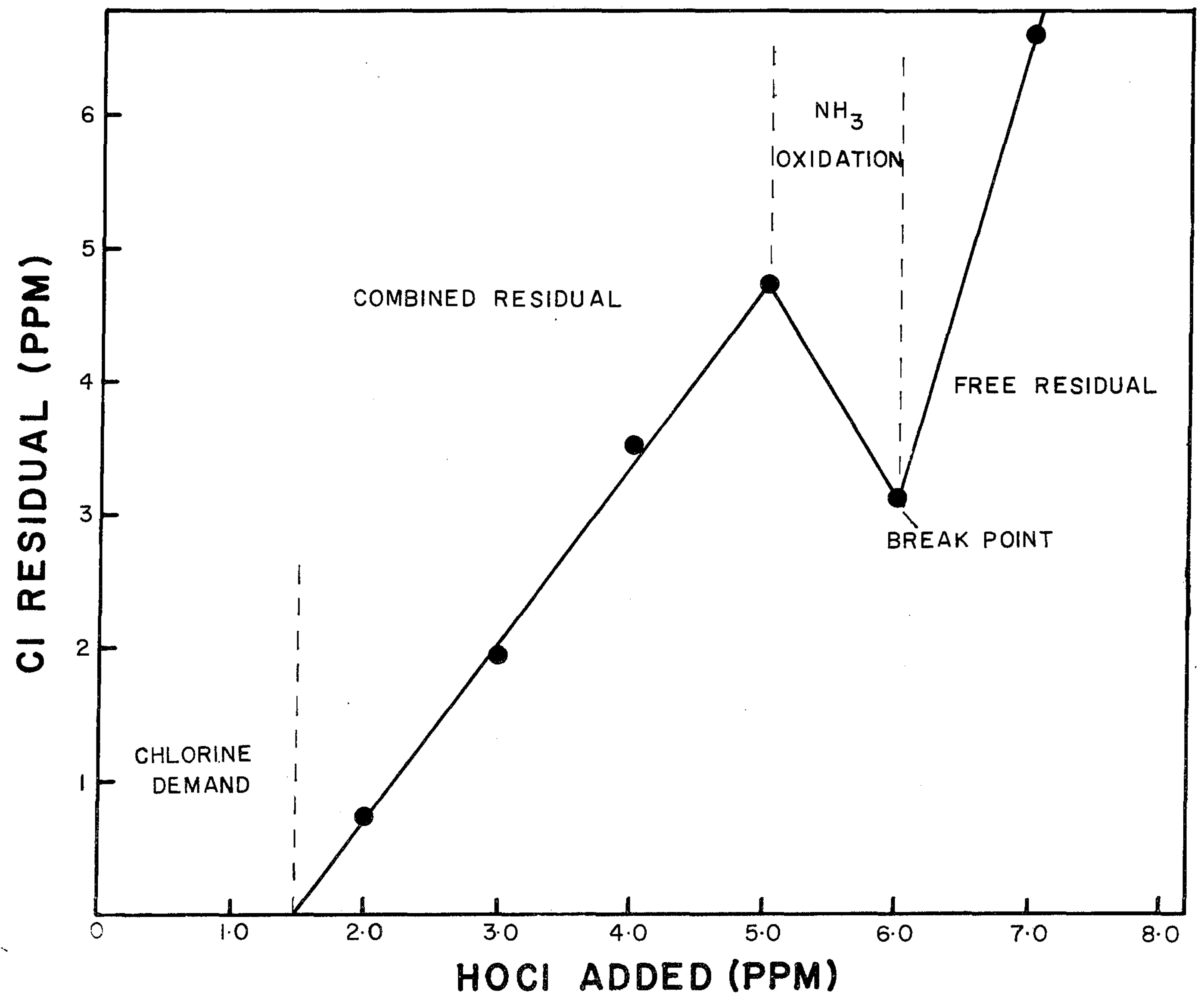

Figure 11. Breakpoint curve for the chlorination of seawater.

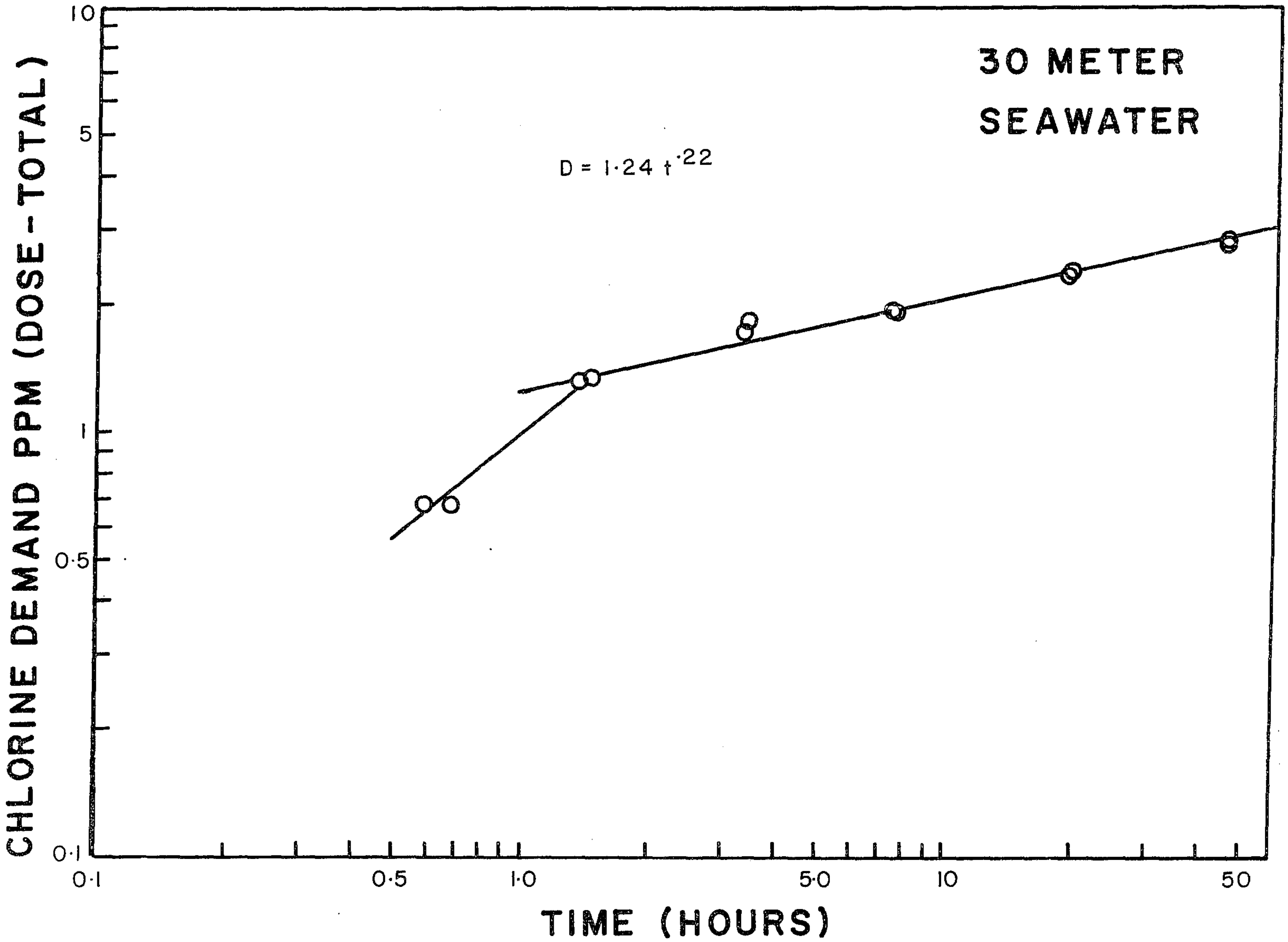

Figure 12. Chlorine demand as a function of time for 30 meters seawater.

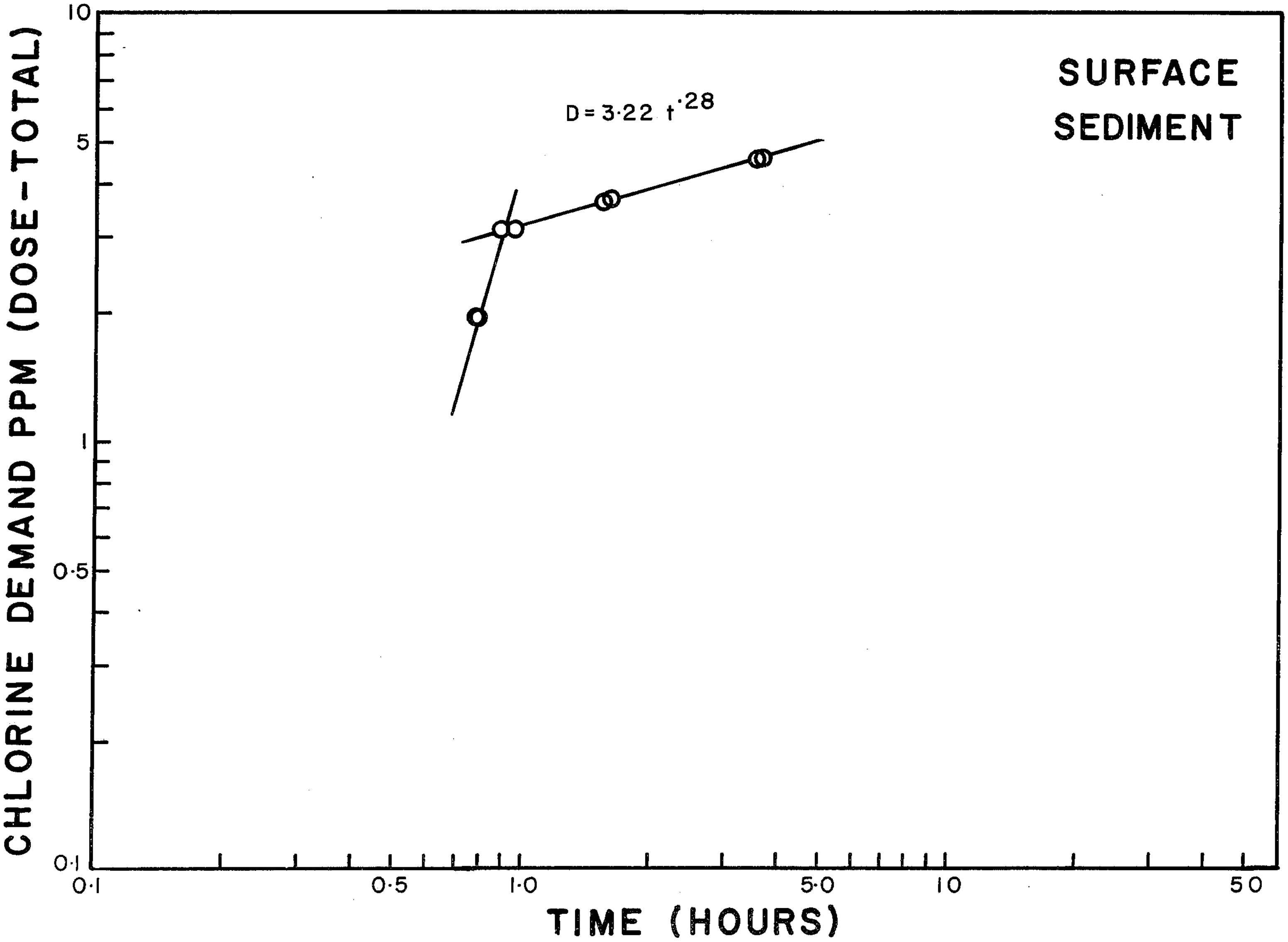

Figure 13. Chlorine demand as a function of time for some Georgia Strait surface sediment.

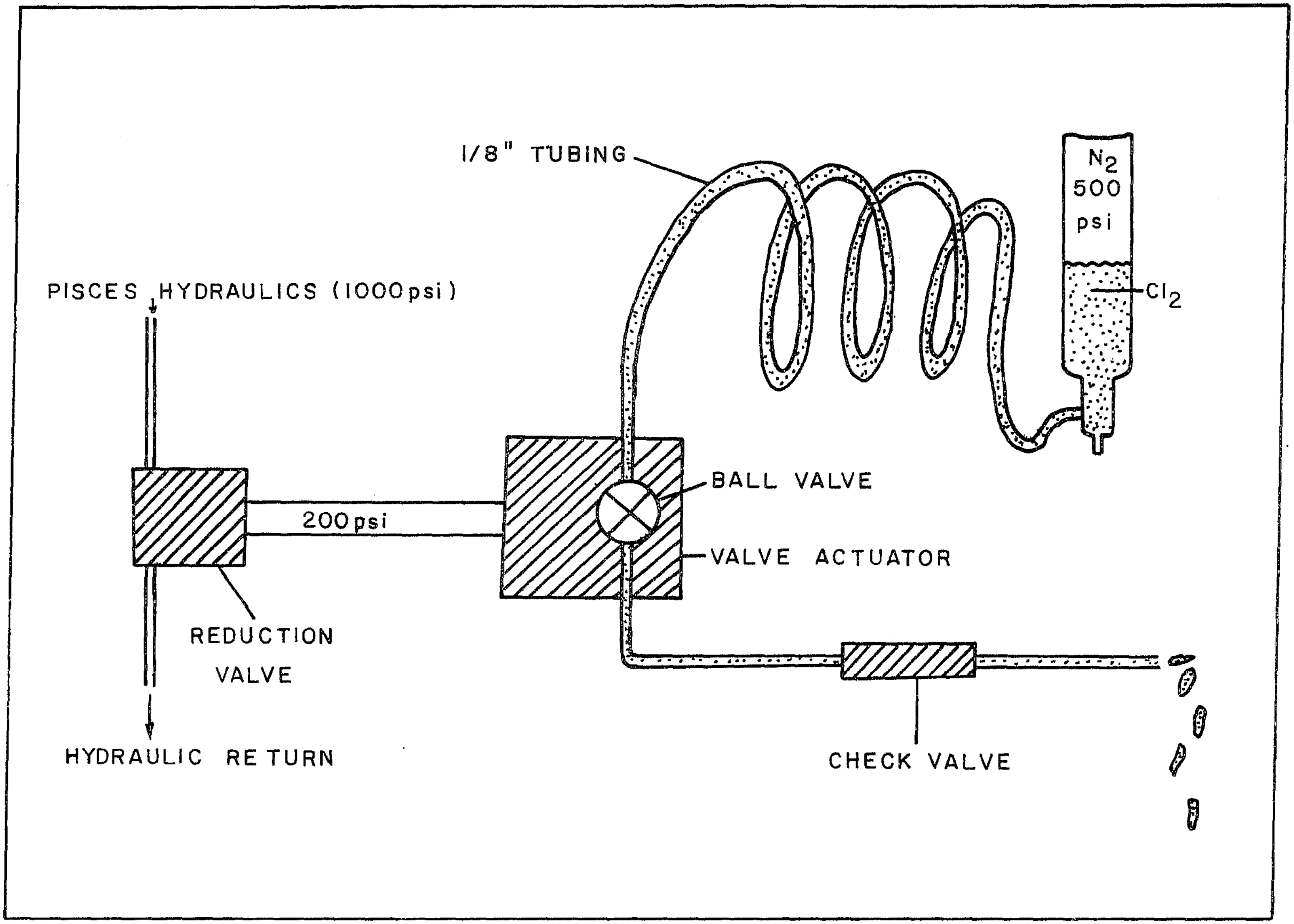

Figure 14. Schematic diagram of the equipment used to release small amounts of chlorine from the Pisces at various depths.

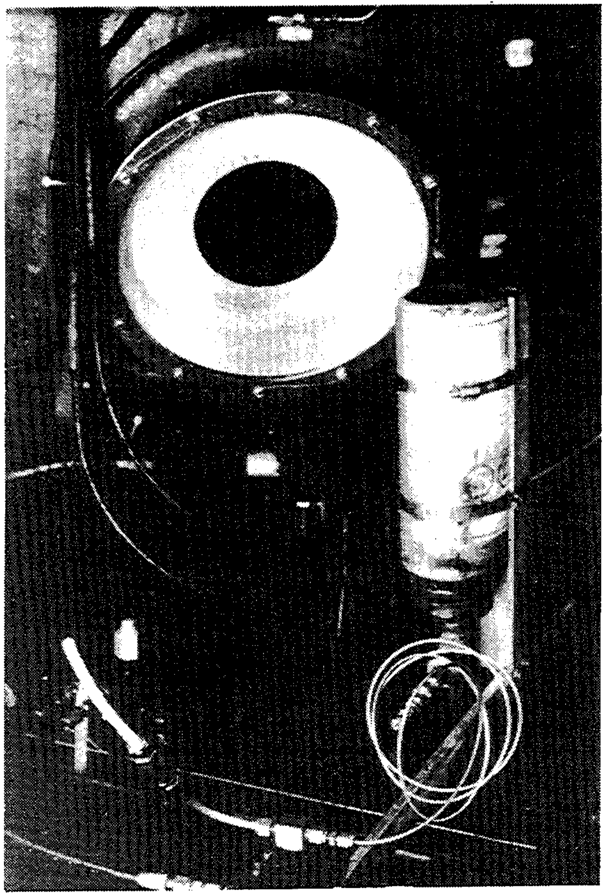

Figure 15. A picture of the equipment on the outside of the Pisces.

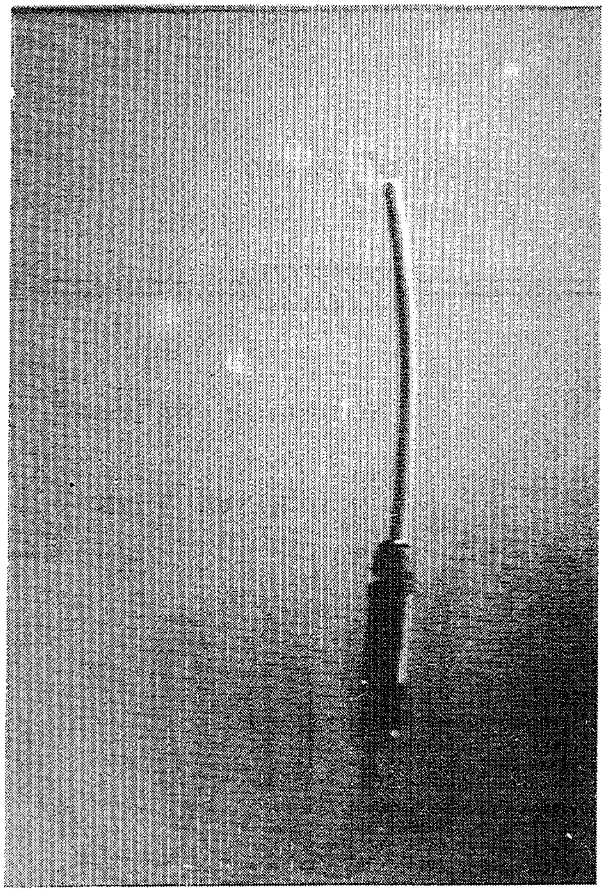

Figure 16. Liquid chlorine drops sinking in seawater at about 145 meters depth.

Figure 17. Liquid chlorine drops sinking in seawater at about 90 meters. Yellowish hydrate can be seen forming on some of the drops.

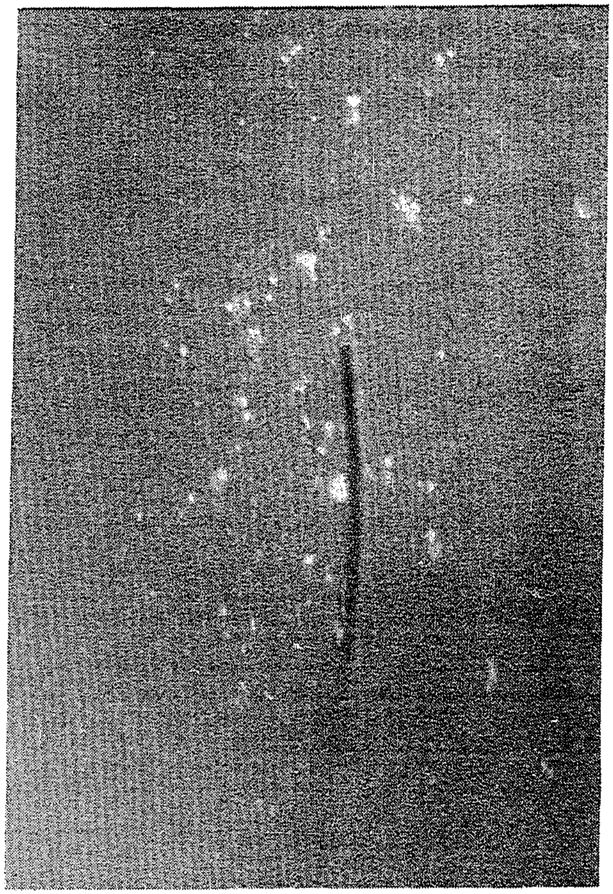

Figure 18. Chlorine in seawater at about 90 meters a short time after injection. Clumps of liquid chlorine and hydrate can be seen in the water.

Figure 19. Chlorine plume at 60 meters. Liquid chlorine drops with hydrate attached are visible to the right of the tube above and below the nozzle.

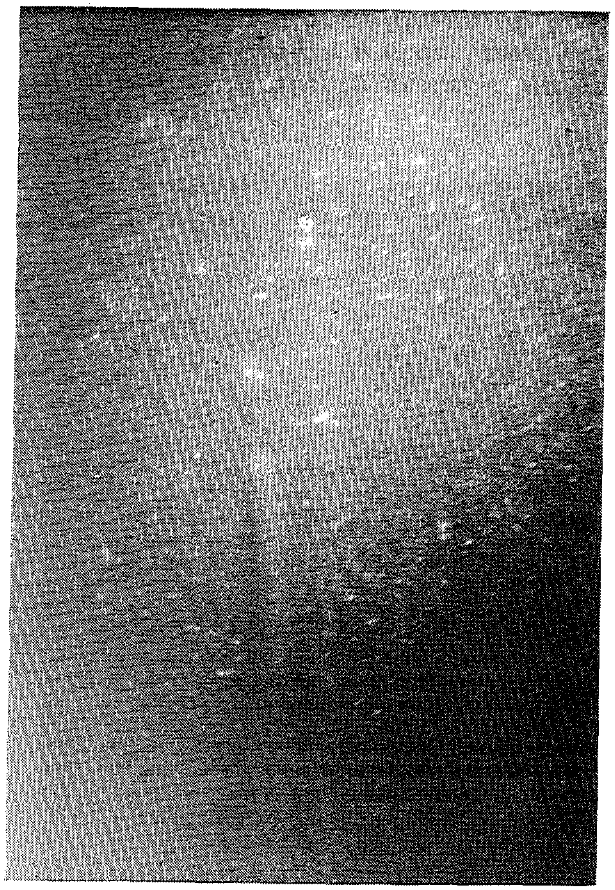

Figure 20. Fine flakes of hydrate generated shortly after chlorine release at 45 meters. Flakes similar to those also seen at 60 meters and 90 meters.

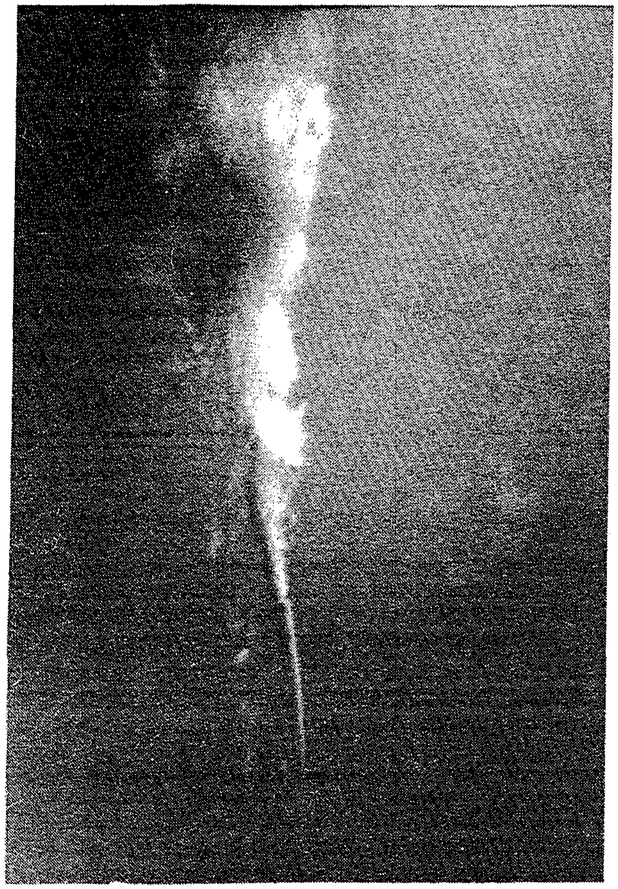

Figure 21. Plume of gaseous chlorine at 25 meters.

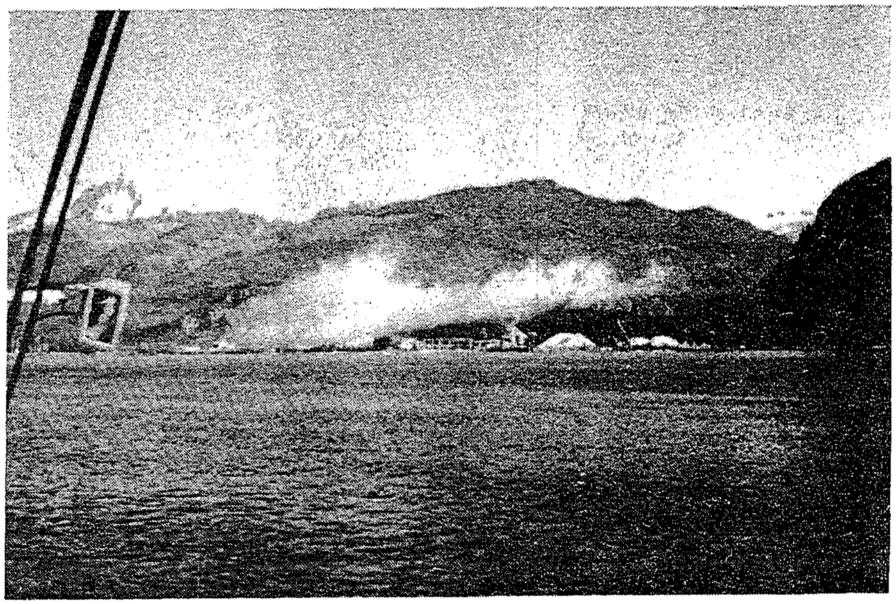

Figure 22. Chlorine "cloud" at Squamish shortly after an accidental discharge from FMC.

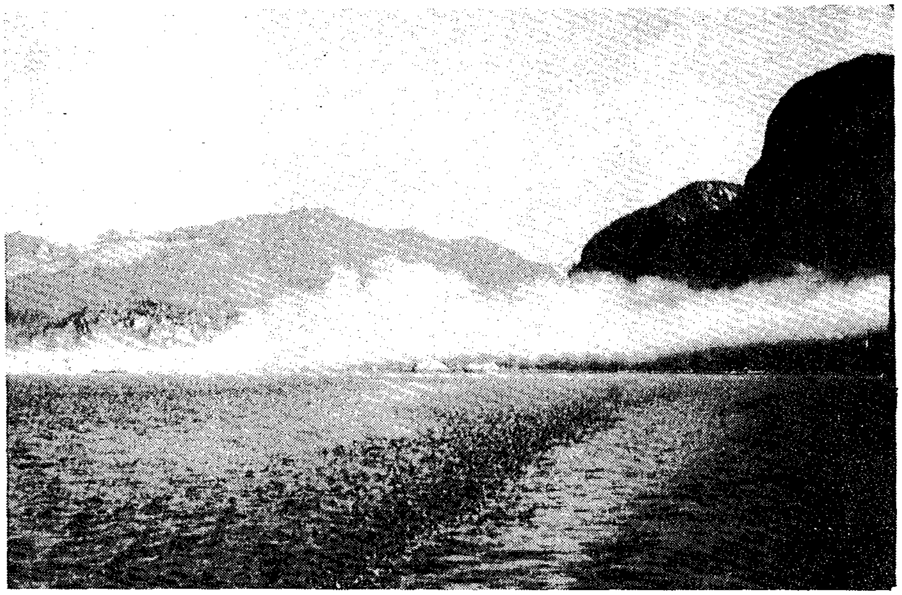

Figure 23. Elongated chlorine cloud about half an hour after the release.

Figure 24. Chlorine mist hanging above the waters of Howe Sound about three hours after the release.

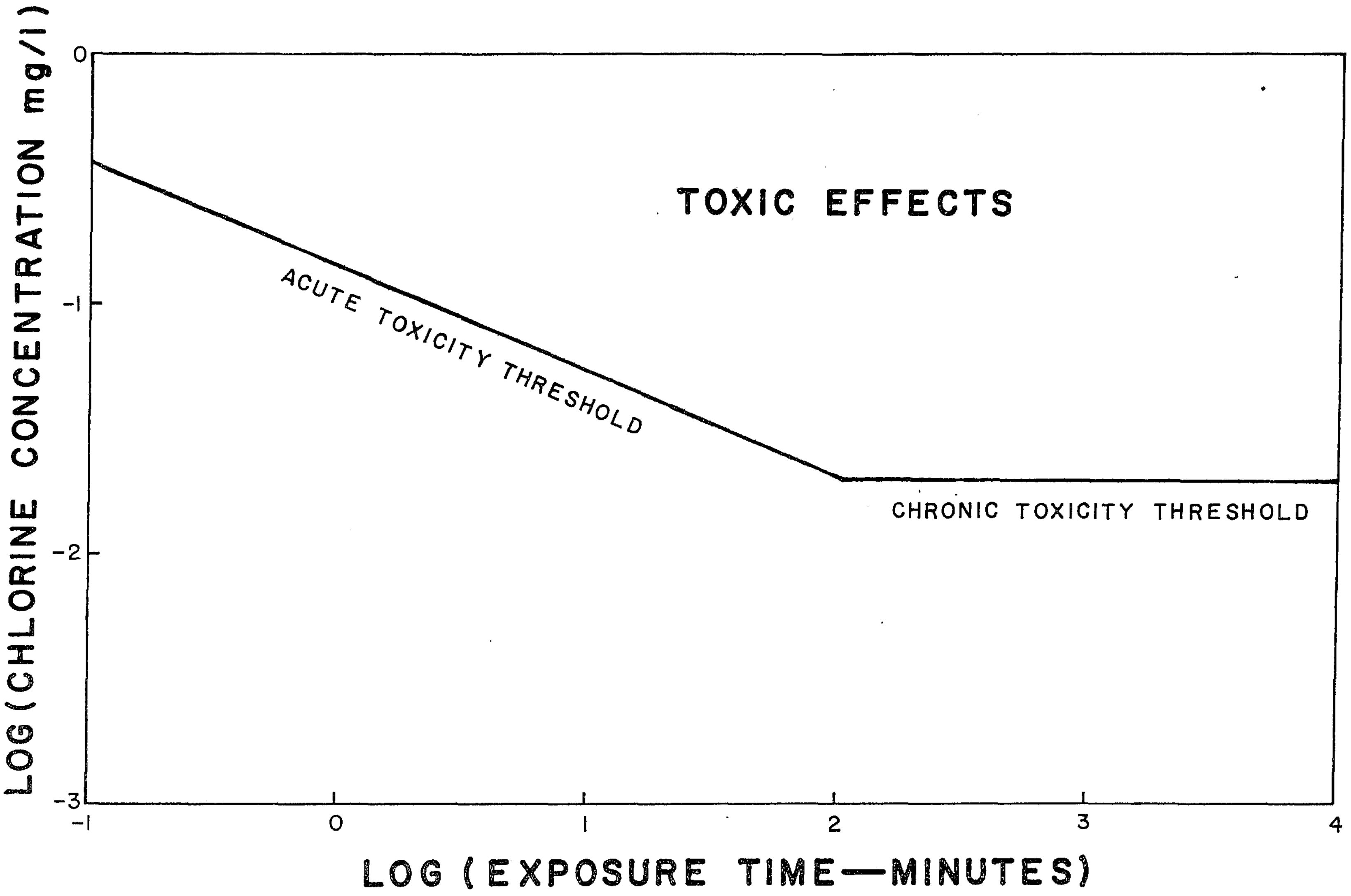

Figure 25. Acute and chronic toxicity thresholds for chlorine in seawater.