

CHLORINE CONTAINER EXPERIMENT

T. DOKTER*

Akzo Zout Chemie Research, Hengelo (The Netherlands)

J.P. BRUNINK

Akzo Zout Chemie, Hengelo (The Netherlands)

H. EGDELTE

Akzo Engineering, Arnhem (The Netherlands)

and Th. KRAMER

Rijkswaterstaat, Directorate North Sea, The Hague (The Netherlands)

(Received September 2, 1984; accepted in revised form November 28, 1984)

Summary

To investigate the effects of the destruction of a chlorine cylinder containing 1000 kg of chlorine, lost by a vessel and residing on the bottom of the sea at a depth of approximately 25 m, some experiments were carried out. The results of these experiments are reported in this paper. The main conclusion is that the container can be destroyed safely with a heavy explosive charge, provided that the area that can be cleared from ships is sufficiently large. The experiments have shown that a circular area around the source with a radius of approximately 10 km should be large enough.

Introduction

To investigate the effects of the destruction of a chlorine-containing eurotainer (see Fig. 1), which was laying at the bottom of the sea as the result of a transport accident which occurred in 1979, a full-scale experiment was performed in 1983 with a recovered container that was dumped again. The results of this experiment are reported here. The main purpose was to study the behaviour of the chlorine cloud that was formed, and to get an estimate of the amount of chlorine that would dissolve in seawater. The potential formation of chlorohydrate (a solid chlorine–water compound) was also of interest.

Two possibilities for performing a test in which the contents of a 1000 kg container could be released were considered. The first was to puncture the container, resulting in a small hole in the gasphase through which the chlorine can leak away as vapour that may dissolve in seawater. The second possibility was

*Present address: Methanor v.o.f., P.O.Box 109, 9930 AC Delfzijl, The Netherlands.

to destroy the cylinder completely and instantaneously by detonating a heavy explosive charge on it.

One experiment only could be performed. It was decided to carry out the complete destruction since the risks involved for the observers were smallest. Instrumentation was poor due to the difficult conditions, the test location being away from the coast and outside the main shipping areas. A detailed study of the behaviour of chlorine in seawater was reported in Ref. [1]. Due to the scale of the test and the instrumentation problems we did not check these results.

The experiment was performed by and under the responsibility of the Directorate North Sea of Rijkswaterstaat with the M.V. *Smal Agt*. As to chlorine handling and safety measures concerning the toxicity of chlorine, assistance was rendered by Akzo Zout Chemie specialists, while the vapour cloud calculations were carried out by a specialist of Akzo Engineering.

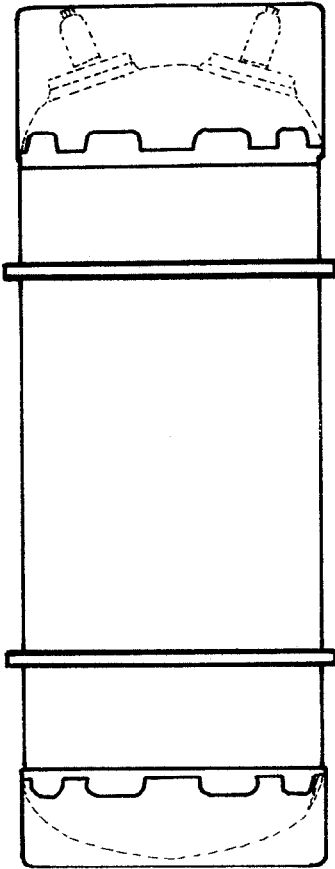


Fig. 1. Chlorine container used in the tests.

Prediction of the results

Potential test results were evaluated to get an idea of the risks involved, both for the experimental crew and for ships that were accidentally present near the test area, especially downwind of it.

The first possibility was to shoot a hole of approximately 8 mm in the cylinder to allow the chlorine to evaporate in a controlled manner. In this case, the emission rate of chlorine through the hole is determined by the heat transfer to the cylinder. The conclusion was that the experiment would last for more than 8 hours, creating great danger to the experimental crew because of a possible shift in wind direction, and because the tide-stream would change during the experiment. Also, the cylinder would start to rise in the water when it still contained approximately 390 kg of liquid chlorine. This would cause great danger because the floating chlorine-emitting cylinder would be uncontrollable.

In the second case, the destruction had to be complete at once. The cylinder should be located at a depth of approximately 25 m. An explosive charge of approximately 6 kg of Donarit S was to be placed onto the container under the skirt on one side.

Upon detonation gas from the explosives will develop at the same time as the container is destroyed. The amount of gas formed by the explosive will be approximately 9 m³ at atmospheric conditions and approximately 3 m³ at the sea bottom, assuming that by intensive mixing with water the temperature will be the same as that of the surrounding water. This gas bubble will probably start to rise before the mass escape of chlorine takes place.

Assuming that the end of the container will be completely cut off, thereby dividing the container into two unequal parts that are forced apart, the chlorine will be finely dispersed in the water. Because of this dispersion, a very large surface area is in contact with water, so the chlorine will evaporate quickly. A volume of approximately 69 m³ of seawater, being lowered 1°C in temperature, is sufficient to let evaporate all of the chlorine. Both bubbles, one consisting of explosives gas and the other of chlorine, will rise quickly towards the surface of the sea. The diameter to height ratio of the bubbles being assumed to be two to one, the initial diameter of the explosives gas bubble will be approximately 3 m while the initial dimensions of the chlorine bubble are 9.5 m in diameter and 4.5 m in height.

In Fig. 2 this situation is presented. It is assumed that a flow channel is formed from the cylinder to the surface in which the expanding bubbles are pushed upwards in a plug-flow stream, getting a higher velocity as the separation of initially dispersed water will take place during the rising period and the density differences are getting larger with the rise of the bubble.

A roughly estimated amount of approximately 150 m³ of water may have been in contact with the chlorine cloud. The solubility of chlorine

in water is very low, but assuming a concentration of 1.5 mg of chlorine per litre water, a maximum amount of 225 g of chlorine will be present as a water solution. The remaining 999.8 kg will be inside the gas cloud. It should be remarked that this value of 1.5 mg/l is highly unrealistic, as the real concentration at these short contact times will be much lower (1.5 mg/l is attained after half an hour, and 3 mg/l after 48 hours [1]).

Due to the detonation and the subsequent rising of the bubble, material from the bottom of the sea will be lifted and moved upwards in the slip-stream following the bubble, forming a surface layer of sand and partially chlorinated organic material. The colour of this surface layer could be somewhere between white and brownish-yellow, caused by the colour of the partially chlorinated material. The formation of chlorohydrate is unlikely as there is sufficient heat present to evaporate the chlorine.

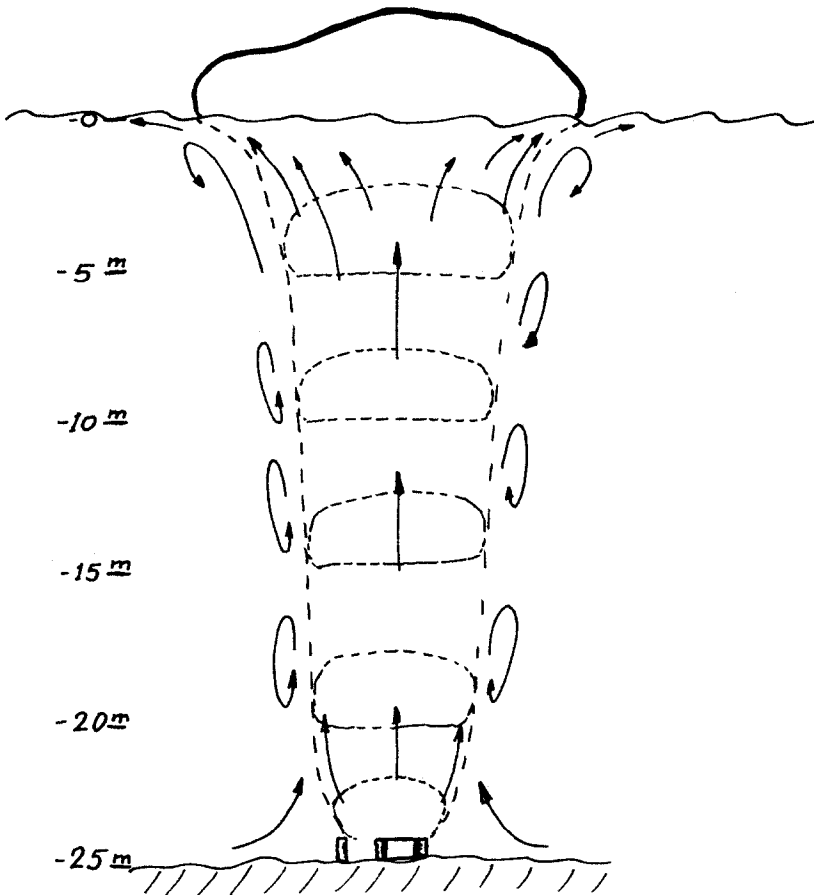


Fig. 2. Estimated situation during the first few moments after the detonation and the subsequent bubble sizes.

Dispersion calculations

The dispersion of the chlorine cloud was estimated using the dense vapour cloud dispersion model of Cox and Roe as well as the Gaussian plume model [2], both for an instantaneous and a continuous point source, using various wind speeds and varying surface roughness to get an indication of potential dangerous situations.

Experimental

Puncturing of an empty vessel

An empty container was used to do some experiments in which the possibility of making a small hole was studied. The surest way, which was, however, the most dangerous to the diver, was to shoot a steel bullet through the wall (8 mm thick) with a gun hammer. The same holds for shooting an airbolt (a hollow bolt that is shot in the wall of the container), that has to be opened by the diver. When the cylinder has corroded too much, the bolt can also be shot through the wall. The conclusion was that this was not the preferred way to puncture the cylinder wall. A similar conclusion was arrived at as to the use of a small explosive charge to puncture the cylinder or to destroy the valve that was mounted on the cylinder.

Complete destruction

A recovered chlorine eurotainer containing 1000 kg of liquid chlorine was dumped again into the North Sea in 1983, secured to a line, with a heavy chain to prevent the cylinder from drifting, and a float to mark the dumping spot. Two more floats were placed at distances of 82.5 m and 280 m downwind behind the container (see Fig. 3). An explosive charge

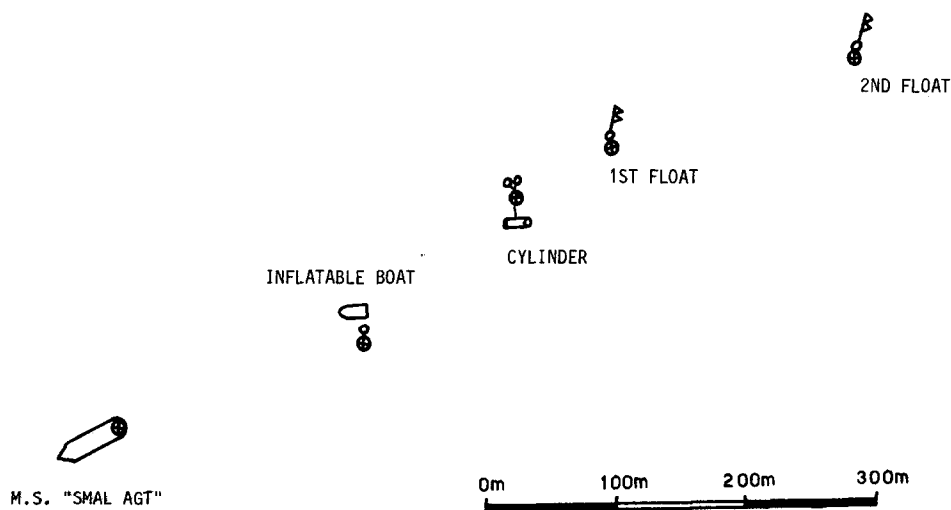


Fig. 3. Locations of ship and cylinder.

of 6 kg of Donarit S was placed under the skirt of the cylinder by a diver and an ignition line was led to a fourth float at a safe distance, where the diving crew was. From cylinders at the upper rear deck of the *Smal Agt* a continuous stream of ammonia was released to help in the visualization of the chlorine cloud.

Due to the rather rough sea surface, a scheme for measurement of concentrations inside the cloud, planned to be performed from rubber boats, was abandoned at the last moment and only visual observations were made from the upper deck of the ship. The distance from ship to cylinder was 351 m.

The relevant conditions during the test are shown in Table 1. The stability class on a sea surface cannot be determined in the same way as on a land surface. According to Nieuwstadt [3], the atmosphere is usually neutral to very stable, and for the test situation class D should be appropriate. From experiments it is known that the roughness of a sea surface which should be used in dispersion calculations is approximately 1 mm, independent of the wave height.

TABLE 1

Relevant test conditions

Wind velocity	8.5 m/s
Wind direction	255 degrees (west-southwest)
Air temperature	6.1°C
Barometer reading	995.5 mbar
Water temperature	5.3°C
Cloudiness	0-2/8
Wave height	1.3 m significant, maximum height 1.8 m
Stability class	D (Pasquill)
Surface roughness	~ 1 mm

At neap tide (water flow velocity zero) the charge was detonated, and after a few seconds the first (clear) gas bubble came up, immediately followed by an intensive grass-green chlorine cloud. This green colour remained visible during the first period of 25 s (approximately 200 m drift of the cloud). It then gradually turned into a white cloud, formed due to reaction with ammonia resulting in a dispersion of ammoniumchloride.

From the first seconds of the emission photographs were taken and a 16 mm film was made. Due to film transport problems the pictures are not sharp, but the moment of detonation and the diameter of the white froth ring on the sea surface are clearly visible, allowing an exact timing of the photographic pictures taken (see Figs. 4-6).

An aeroplane, assisting in following the cloud on its journey over the sea, was also used to take pictures of the test site before and after the detonation, and of the cloud at various times up to about 26 min, after which it was no longer possible to trace the cloud. The aeroplane also viewed the cloud just after emission by infrared and ultraviolet spectros-



Fig. 4. Gas bubble 0.8 s after the detonation.



Fig. 5. Gas bubble 2.2 s after the detonation.

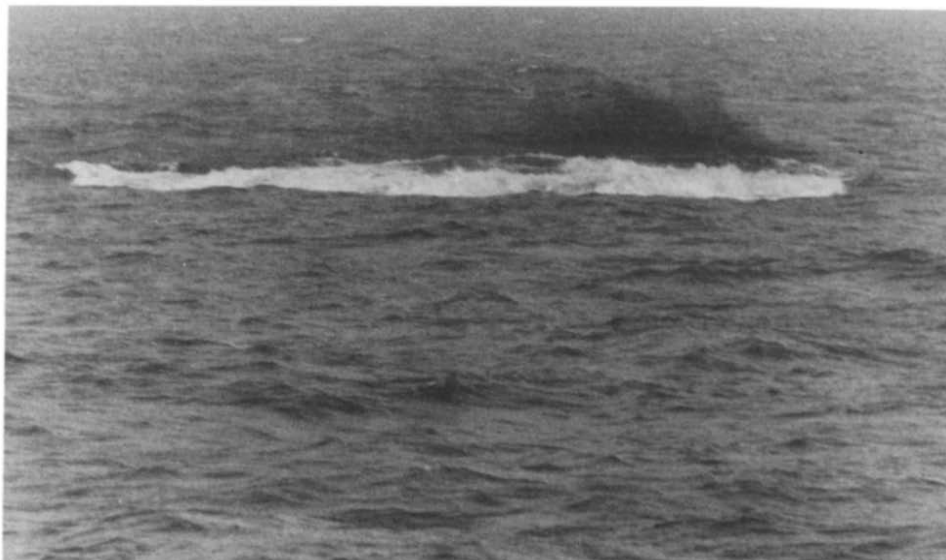


Fig. 6. Gas bubble 3.9 s after the detonation.

copy; however, it was not possible to detect the cloud using these techniques. From the infrared recording, which is capable of making very small temperature differences visible, it can be concluded that the chlorine was at ambient temperature, at least shortly after the emission, while no large floating pieces of chlorohydrate were detected.

Results

The following results were obtained:

- The detonation took place at 14 hours, 09 minutes and 35 seconds.
- Between the time of detonation and the cloud breaking through the surface 1 to 1.5 s elapsed.
- The cloud was fully above sea level within 3 s after the detonation.
- According to the pictures, the first bubble (explosives gas) had a diameter of less than 7.5 m, whereas a diameter of approximately 3 m was reported by the plane crew. This may be compared with our estimation of 3 m.
- The initial chlorine bubble had a diameter of approximately 15 m (estimated, 9.5 m). At a second turn, the plane reported a cloud of 30 m in diameter. The initial height was approximately 3 m.
- From the sizes of the chlorine cloud it may be concluded that nearly all chlorine was inside the cloud and only very little chlorine had dissolved in the water.
- The chlorine came up in one big bubble.
- No formation of chlorohydrate was observed, neither by infrared or ultraviolet spectroscopy, nor visually.

- No dead fish were noticed.
- After 200 m travel the color of the cloud changed from greenish yellow to yellowish white due to reaction with ammonia released from the upper deck of the *Smal Agt*.
- The cloud in its entirety drifted with the wind and rose shortly after emission above the sea level. There was no visible contact between the sea and the cloud.
- From the ship the cloud could be seen for approximately 10 min, having travelled a distance of over 5 km. The aeroplane followed the cloud for 25 min (8.37 km of cloud travel in 16 min).
- In Fig. 7 the sizes of the visible part of the cloud, as seen by the crew in the aeroplane are given, together with the calculated shape of the cloud at different times. The concentration at the outer edge of the visible cloud is unknown.
- The place of the emission was clearly visible as a bright green spot surrounded by a white froth ring. From the fact that after some 60 min sea gulls started fishing in the spot and landed on the water surface, the conclusion can be drawn that in the air just above the sea the chlorine concentration was much lower than 1 ppm. After more than one and a half hour the spot was still visible, but chlorine could no longer be detected above the seawater (Draeger test tube). Figure 8 presents the sizes of the froth ring as a function of time. In Fig. 8 two different lines are given, one obtained from the photographs and the other from the

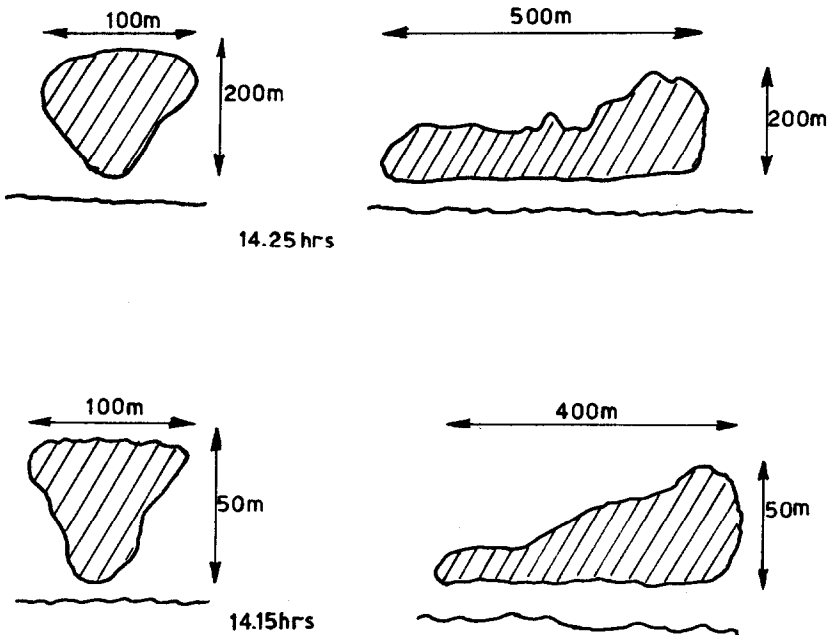


Fig. 7. Cloud shapes as seen from the aeroplane at 322 s and at 930 s.

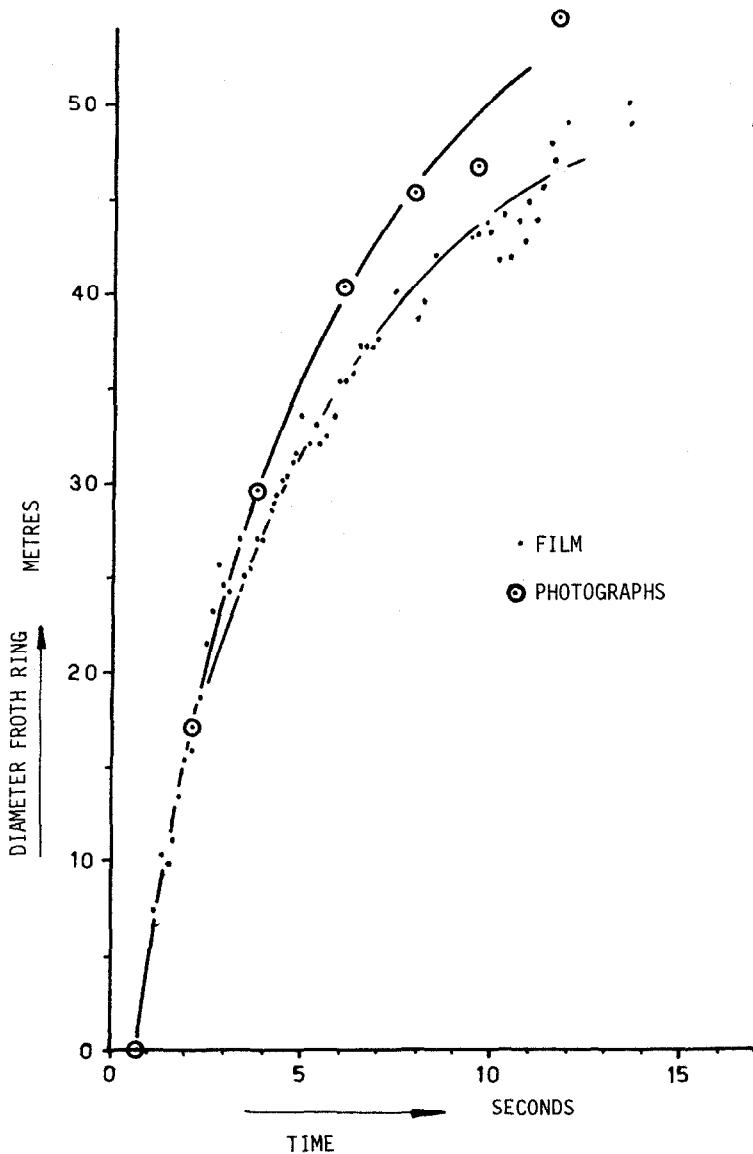


Fig. 8. Dimension of froth ring as a function of time.

film. Due to problems with the camera only the horizontal dimensions are visible; however, correct timing was possible.

Calculation of dispersion

For calculating the dispersion, the following starting points were used: The instantaneous source is the cloud at the moment that it has a diameter

of 30 m and a height of 2.5 m. At that moment the volume is 1800 m^3 : 1000 kg chlorine has a volume of 320 m^3 , the initial dilution is about six times, while the average density of the cloud is 1.24 times the density of air.

Initial dispersion

A cloud with a relative density of 1.24 should behave like a dense vapour cloud (as it actually is) and, therefore, show gravity spread. This was not observed in this experiment. If it occurred, the effect was probably obscured by dilution at the cloud boundaries.

To calculate initial dispersion the dense vapour cloud dispersion model of Cox and Roe [2] was used. For subsequent dispersion the Gaussian plume model was used, with parameters as suggested in Ref. [4]. For distances of more than 1000 m the results are not significantly different from

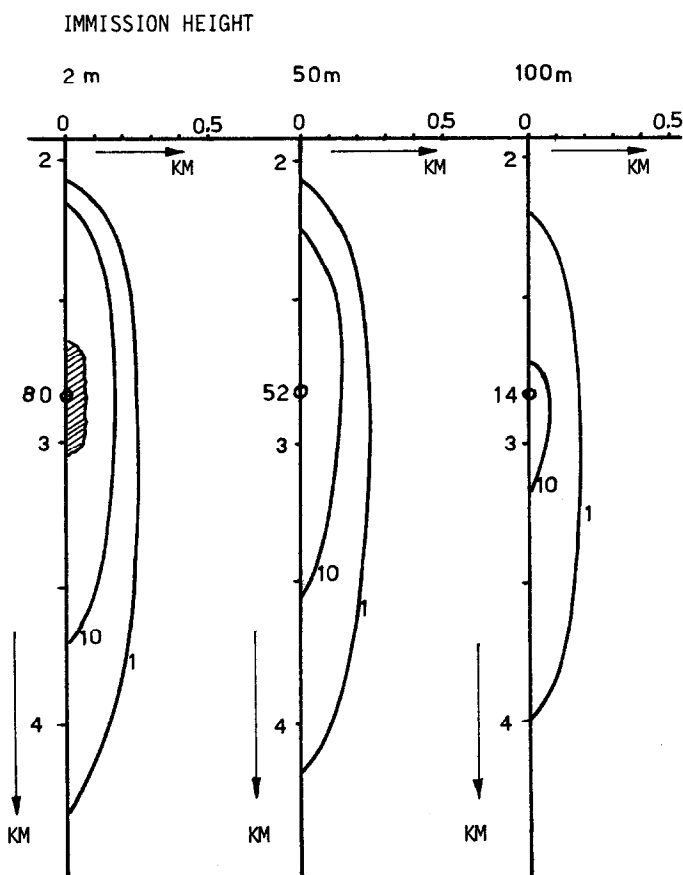


Fig. 9. Calculated and visible dimensions of cloud (at 322 s) for immission heights of 2, 50 and 100 m; concentration figures in milligram per cubic metre.

those obtained with the Gaussian plume model alone, so in our situation the latter method could be used predominantly.

The results of the calculations, using the experimental conditions stated above, are presented in Figs. 9—12. The shaded areas in the figures represent the cloud as observed by the aeroplane crew. As can be seen, the results of the calculation are in good agreement with the visual observations from the aeroplane, although the visible part of the cloud was determined not only by the dispersion of the chlorine, but also by the concentration of ammonia throughout the cloud.

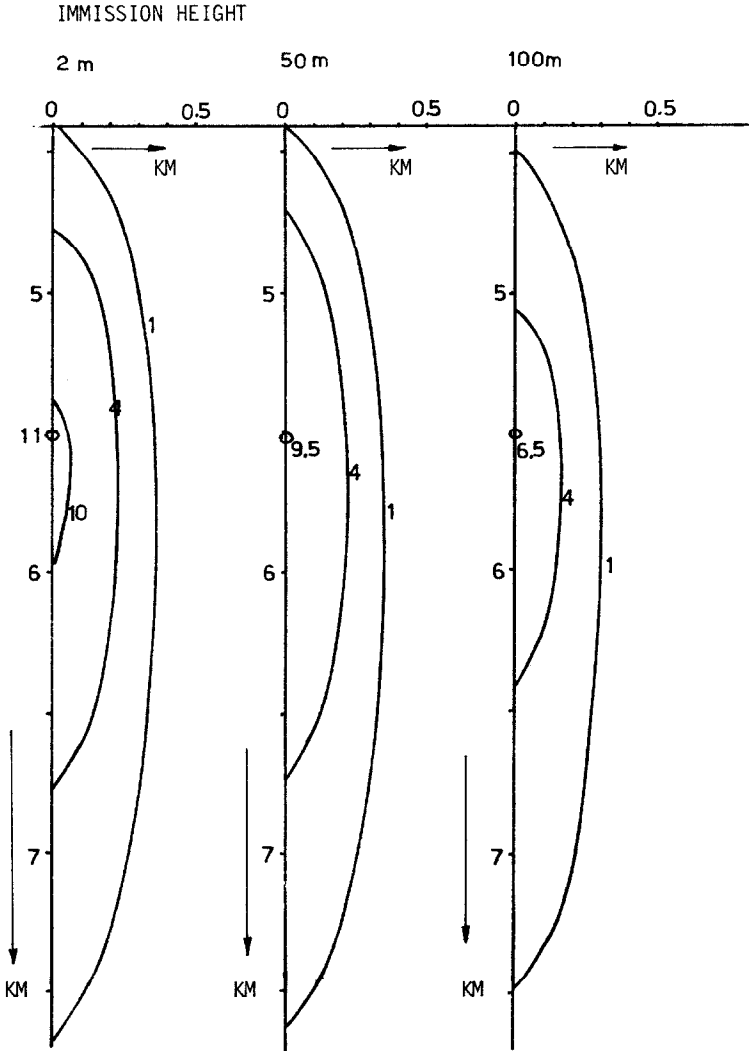


Fig. 10. Calculated dimensions of cloud (at 682 s) for immission heights of 2, 50 and 100 m; concentration figures in milligram per cubic metre.

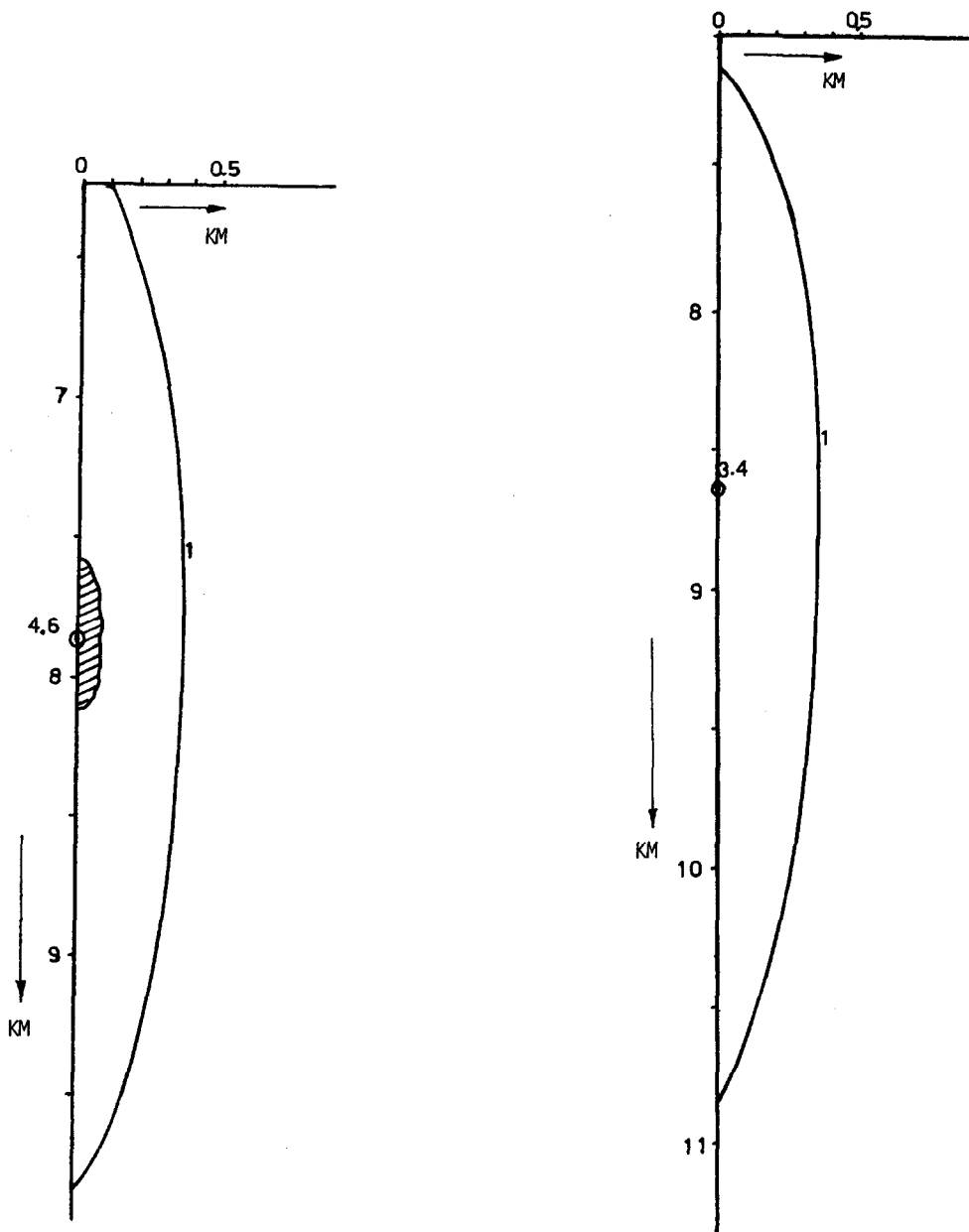


Fig. 11 (left). Calculated and visible dimensions of cloud (at 930 s) for an immission height of 2 m; concentration figures in milligram per cubic metre.

Fig. 12 (right). Calculated dimensions of cloud (at 1050 s) for an immission height of 2 m; concentration figures in milligram per cubic metre.

When a limit concentration of 4–10 mg/m³ (1–3 ppm) is allowable, the chlorine cloud should be sufficiently diluted at a distance of 5 to 6 km, and in general 10 km should be considered a safe distance under the test conditions.

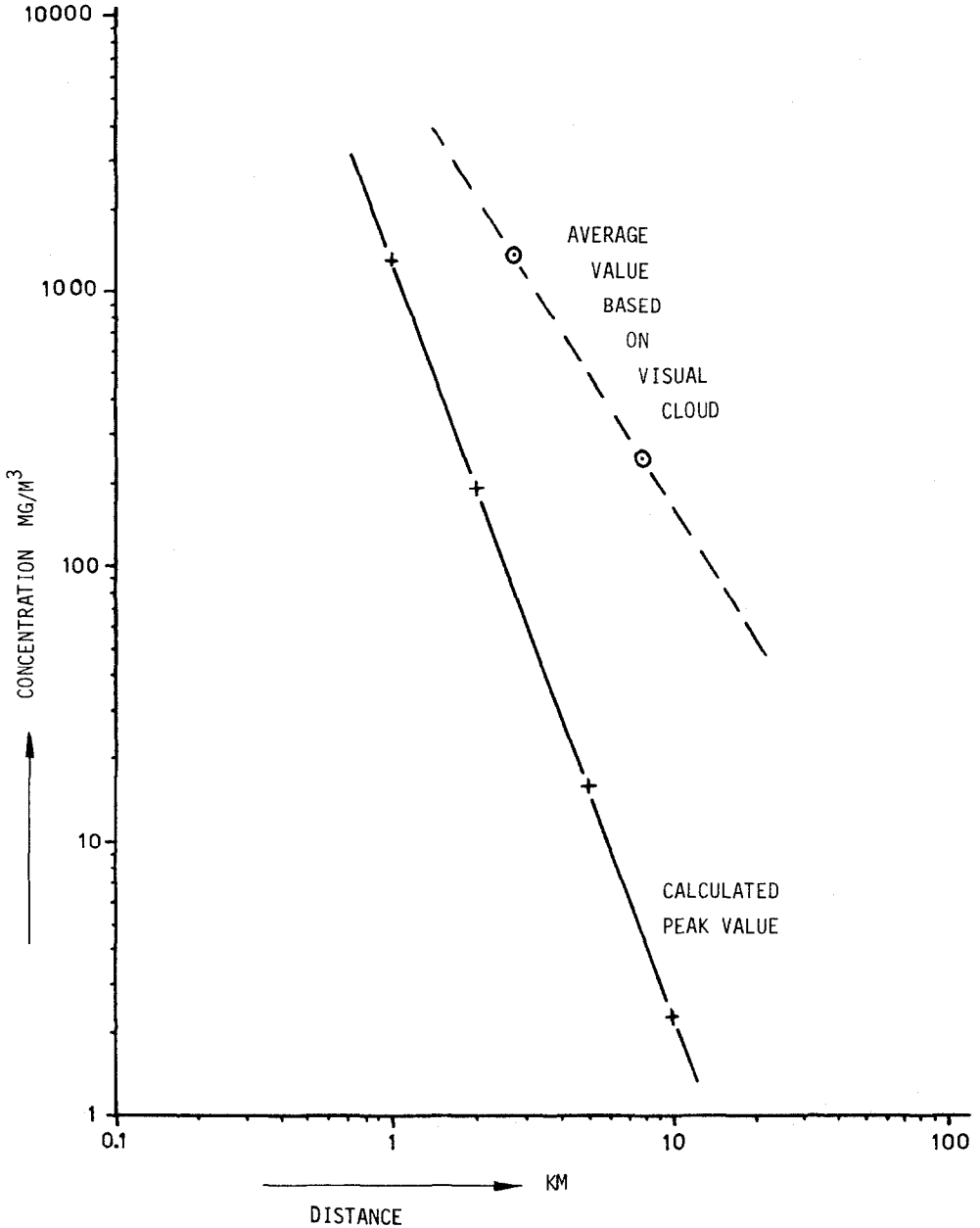


Fig. 13. Calculated peak concentration and maximum average value (based on visible dimensions) as a function of time.

In Fig. 13 the peak concentrations of the cloud are given as calculated by the dispersion model. The average concentration, as shown by the dotted line in Fig. 13, is the total amount of chlorine (1000 kg) divided by the visual cloud volume. This line shows, of course, much too conservative an estimate, as no dispersion outside the visible cloud is assumed, which is highly unrealistic. In Fig. 14 the visible cloud dimensions, measured from the photographs and estimated by the crew of the aeroplane, are given.

It is useful to keep in mind that the actual wind velocity hardly influences the chlorine concentrations. This follows from the fact that, given the stability class, in the Gaussian plume dispersion model for instantaneous sources concentrations are independent of wind velocity. The toxic effect, however, is proportional to the reciprocal of the wind velocity since it is proportional to exposure time.

In the calculations the following conservative elements have been included: No correction was made for dissolution or reaction of the chlorine with the sea surface (this is correct in view of the very low solubility of chlorine in seawater [1]). It was assumed that the full amount of 1000 kg was present in the initial cloud of 1800 m³.

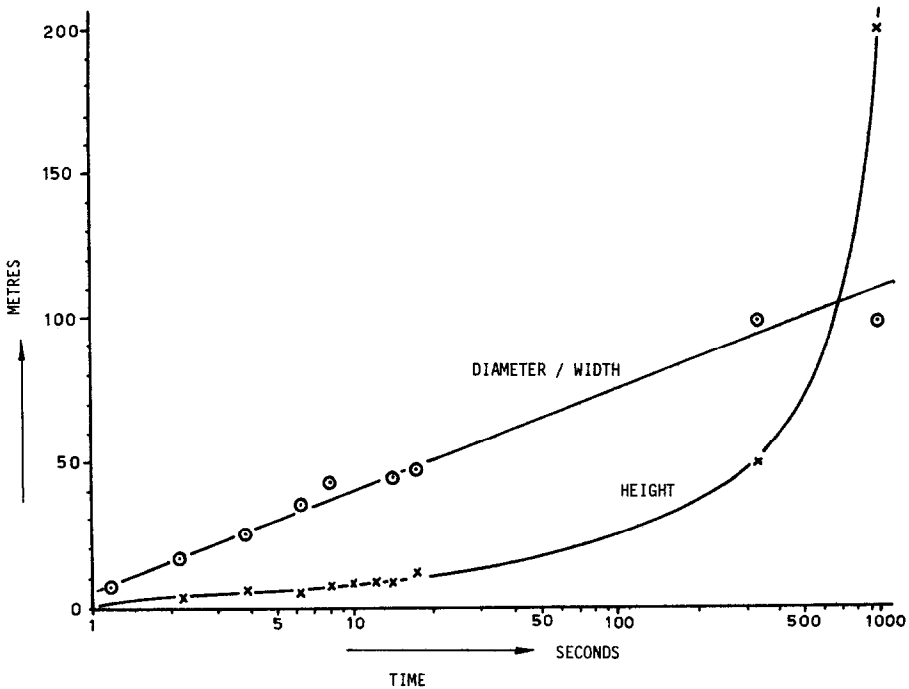


Fig. 14. Visible cloud dimensions as a function of time.

Conclusions

From the experiment and the calculations it can be concluded that if a distance of approximately 10 km around the location of the container is kept free from shipping, the destruction of the chlorine cylinder can be performed without danger to the crew, people at the distance indicated, and the environment.

Little or no damage is noticed other than that directly resulting from the detonating explosive charge. Only a very small amount of chlorine is dissolved in the seawater. The gas cloud disperses without much contact with the sea level occurring. No signs of chlorohydrate formation were noticed during this experiment.

Acknowledgements

The authors wish to thank the crews of the M.V. *Smal Agt* and the aeroplane PH-MPC, and the diving crew of Smit Tak International for their assistance during this test. Thanks are also due to Mr. Stolwerk for his advice and cooperation with the experiments to shoot small holes in a cylinder, and finally to Akzo Zout Chemie's Department of Safety and Environmental Affairs for the use of their chlorine monitor and personal safety equipment.

References

- 1 R.W. MacDonald. The interaction of chlorine and seawater, with special reference to the four liquid chlorine tank cars lost in British Columbia coastal waters, *J. Hazardous Materials*, 2(1977/78): 51-75.
- 2 R.A. Cox and D.R. Roe, A model of the dispersion of dense vapour clouds, Presented at 2nd International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Heidelberg, September 6-9, 1977.
- 3 F.T.M. Nieuwstadt, The dispersion of pollutants over a water surface, Presented at the International Technical Meeting on Air Pollution Modelling and its Applications, Leuven, September 20-23, 1977.
- 4 Methoden voor het berekenen van de fysische effecten van het incidenteel vrijkomen van gevaarlijke stoffen, Issued by Directoraat Generaal van de Arbeid, The Netherlands, 1979.