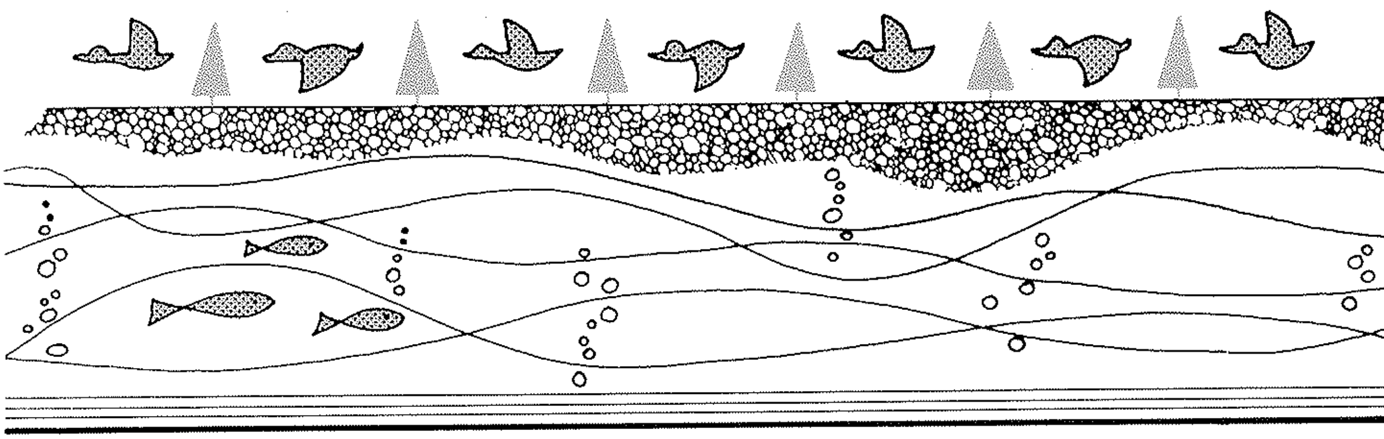
Environment Canada | Environnement Canada

SPILL TECHNOLOGY NEWSLETTER



An informal quarterly newsletter published by the
Technology Development and Technical Services Branch
Conservation and Protection, Environment Canada, Ottawa, Canada

Table of Contents

VOLUME 13 (1)
March 1988

ISSN 0381-4459

Canada

Mr. M.F. Fingas and Mr. K.M. Meikle
Technical Editors
Environmental Emergencies Technology Division
Technology Development and Technical Services Branch
Environment Canada - C&P
River Road Labs
Ottawa, Ottawa
K1A 0H3

Phone (613) 998-9622

Stella Wheatley
Publisher and Coordinator
Technology Development and Technical Services Branch
Environment Canada - C&P
Ottawa, Ontario
K1A 0H3

Phone (819) 953-1193

The Spill Technology Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on spill countermeasures and other related matters. We now have over 2000 subscribers in over 40 countries.

To broaden the scope of this newsletter, and to provide more information on industry and foreign activities in the field of spill control and prevention, readers are encouraged to submit articles on their work and views in this area.

INTRODUCTION

This edition of the Spill Technology Newsletter marks the beginning of the thirteenth year of publication. Readers will note that the newsletter continues the use of a bilingual format begun three issues ago for economic reasons.

The first article is by Mark Burley of Esso Resources and is a summary of a research project to restore land affected by brine spills. Salt water, or brine, is often produced with oil at production sites. The brine, which varies in salinity from that of seawater to values much higher, is separated from the oil at the well site or at production batteries and reinjected into the formation both to aid in recovery of oil and to dispose of the brine. Over several years, hundreds of brine incidents have been recorded in Canada's spill records. These spills are difficult to deal with, particularly in arid areas. Mark Burley's article describes several treatments used to restore such agricultural land. The best salt removal rate was for plots treated with gypsum, ammonium nitrate and manure, and also managed with soil ripping and flushing during the summer period.

The second article is by Carol Ann McDevitt and coworkers who describe research on boiling liquid expanding vapour explosions (BLEVE's). The University of New Brunswick researchers have found that the superheat temperature limit cannot be used to predict the occurrence of BLEVE's as once thought, but that there are other physical parameters that may be relevant. Fireball formation is found to be independent of BLEVE formation. The occurrence of the BLEVE is also found to be independent of rupture location.

REPORTS AND PUBLICATIONS

The "Bibliography on the Fate and Effects of Aquatic Oil Pollution" has been completed by Seakem Oceanography. The bibliography has over 7000 citations cross-referenced to key words and author. Emphasis is placed on physical, chemical and biological effects on marine and freshwater ecosystems. The bibliography is available in soft cover, 688 pages for $190 and on 5 1/4 inch floppy diskettes for $190. Order from Seakem Oceanography Limited, P.O. Box 696, Dartmouth, Nova Scotia, B2Y 3Y9, or phone Fred Guptill at (902) 463-0932.

The Environmental Emergencies Technology Division has released the following manuscript reports. For copies contact: Environmental Protection Publications, Conservation and Protection, Environment Canada, Ottawa, Ontario, K1A 0H3.

1. "Report on the In-Tank Mixing Studies" (EE-100)

2. "A Person-Portable Analytical System for the Determination of Polychlorinated Biphenyls" (EE-99)

3. "Evaluation of Wright and Wright Oil Film Monitor for Detection of Offshore Chronic Oil Discharges" (EE-98)

4. "Evaluation of Sorbent Use for Retrieval of Hazardous Sunken Liquids" (EE-97)

5. "The Transient Submergence of Oil Spills: Tank Testing and Modelling" (EE-96)

6. "Oil Spills in Leads: Tank Tests and Modelling" (EE-95)

7. "Laboratory and Tank Tests of Elastol" (EE-94)

8. "Formation and Stability of Water-in-oil Emulsions" (EE-93)

9. "The Behaviour of Oil in Freezing Situations" (EE-92)

10. "Steam Stripping as an Emergency Countermeasure" (EE-91)

RECLAMATION OF BRINE SPILL SITES

Submitted by: M.J. Burley
Esso Resources Canada Limited
Production Research Department
Calgary, Alberta

Introduction

Salt water (brine) is often produced with crude oil and must be separated from it at a processing facility prior to disposal by deep-well injection. As oil-producing fields have declined in productivity, larger volumes of salt water have been produced. This trend has led to higher pipeline pressures and corrosion rates which has resulted in an increasing frequency of saltwater spills. In response to the situation, oil companies have developed spill cleanup programs that utilize a variety of soil reclamation techniques designed to meet the needs of a number of soil and climatic conditions. An area that has not yet received this kind of attention has been the semi-arid lands of south-eastern Saskatchewan and south-western Alberta in which a number of old producing fields are located.

A brine spill disturbs both the physical structure of the soil and the normal osmotic gradient existing between the soil and plant roots.

The soil structure is sensitive to high sodium chloride (NaCl) concentrations because clay particles behave like a sodium sensitive ion exchange medium. Divalent calcium and magnesium ions are normally bound to the clay surfaces where they act to form clay aggregates. During a brine spill they are displaced by monovalent sodium and after a rainfall they are washed away. The remaining sodium cannot preserve the aggregated state, and disaggregation or dispersion, results. The effect of dispersion is a structural breakdown of the soil (Richards et al., 1969) so that when the spill site dries out it hardens into an impenetrable mass exhibiting restricted gas and water exchange with plants.

High concentrations of NaCl can also reverse the normal osmotic gradient that exists between soil and plant roots (Henry et al., 1979). This gradient is responsible for the transfer of water and nutrients from the soil to the plant. After a spill, vegetation quickly dies from dehydration and nutrient deficiencies. The surface of a dispersed soil is pictured in Figure 1. It shows the characteristic cracks that result from contracting as it dries into tight, impenetrable clumps. Vegetation has died off making the soil susceptible to erosion and loss of nutrients.

Reclamation of contaminated sites traditionally consists of incorporating a calcium source, a fertilizer and an organic amendment such as manure into the topsoil (de Jong, 1977). Rainfall is relied upon to leach the calcium down into the deeper soil layers and to flush the displaced sodium out of the root zone. The role of the organic amendment is primarily to maintain soil permeability and the fertilizer promotes new vegetation growth.

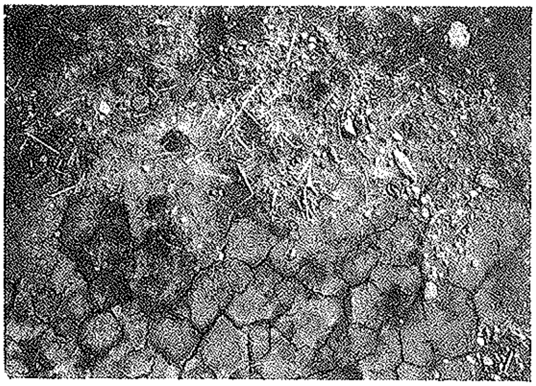


FIGURE 1 PHOTOGRAPH OF A DISPERSED SOIL SHOWING CHARACTERISTIC SURFACE CRACKING, LACK OF VEGETATION COVER AND SALT CRUSTING

The climate and soils of southeastern Saskatchewan represent a particularly difficult reclamation problem. Low rainfall, shallow groundwater and high evaporation rates combine to concentrate salt at the soil surface and maintain it there indefinitely. The soils of this area are often high in clay content and consequently they disperse easily. Many of these soils support some type of agriculture and so an effective reclamation program is needed.

Objective

The objective of this study was to examine amendments and procedures to reclaim brine-affected soils in semi-arid climates. The approach was to conduct a set of field trials to:

a). compare the relative effectiveness of gypsum to Saline Soil Saver (SSS) as an amending source of calcium; SSS is a commercially available product (Bondell Group of Calgary, Alberta) that contains calcium nitrate in solution; it has not been used to reclaim dispersed brine-affected sites in the area before;

b). evaluate the effectiveness of flushing a calcium amended site; and

c). evaluate the possible benefits of soil ripping on salt removal.

Sampling Methodology

Soil amendment performance was measured by soil sampling. Soil samples were collected with a Dutch Auger at three sampling depths, 0 to 20 cm, 20 to 40 cm, and 40 to 60 cm. A composite sample was obtained by combining three random samples per depth from each of the three plots in a given treatment zone. The resulting three analyses per depth for each zone were averaged to give one analysis per depth for each zone.

Site Description

The chosen site is shown in Figure 2 and was selected primarily because it had good drainage. It was located approximately 200 km southeast of Regina, Saskatchewan. The presence of a service road made the location easily accessible and because it was at the edge of a cropped field, studies could be carried out with minimal interference with the adjacent farming operations. The surface terrain was essentially level with a slight slope to the west.

Ten test zones were staked out and labelled A through J. Each zone was 6-m long and 3-m wide and was separated from the next zone by a 1.2-m buffer strip. Each zone was subdivided into three test plots from which soil samples were taken. The plots were 1.2-m square with 0.6-m buffer strips.

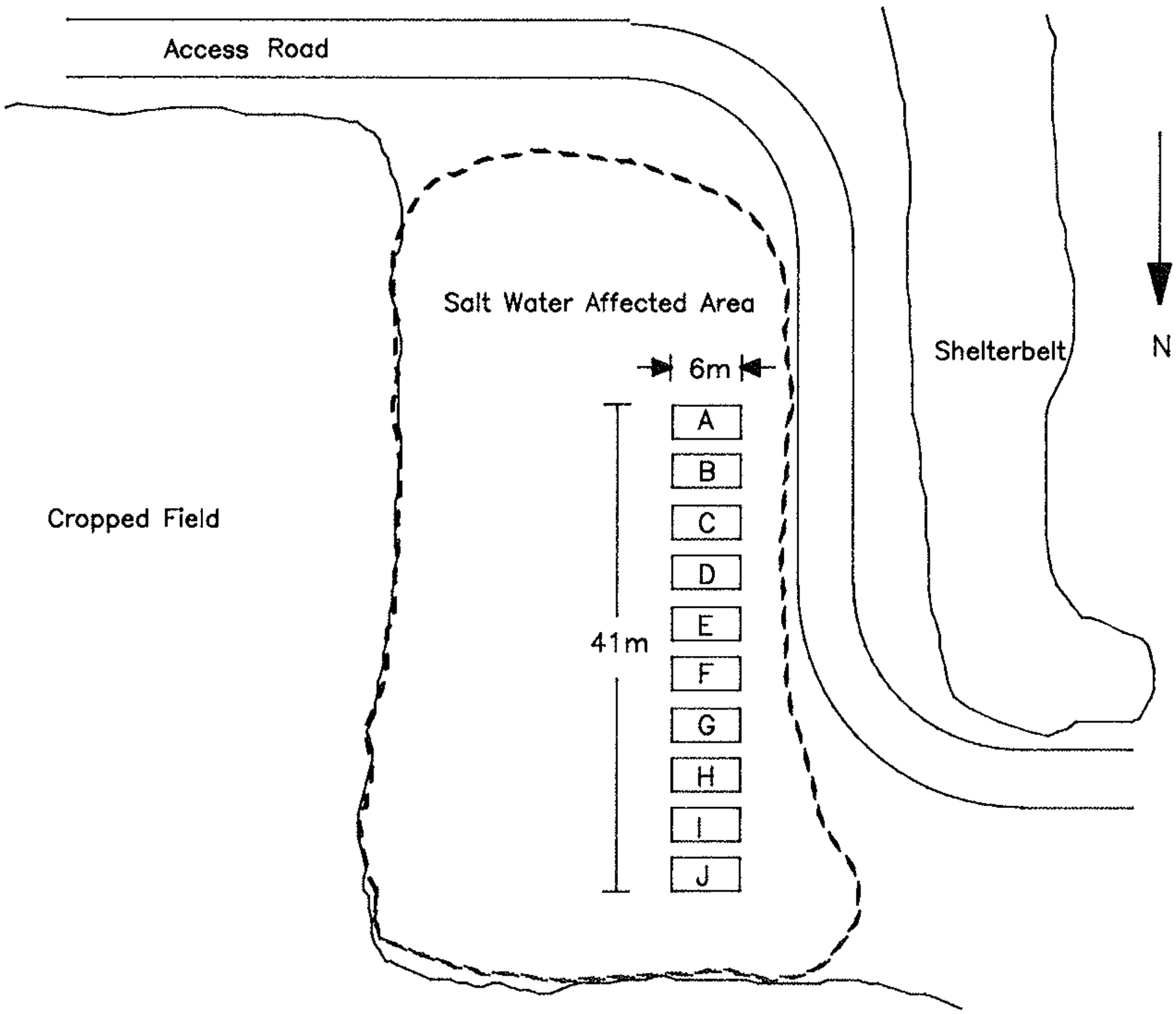


FIGURE 2 SCHEMATIC DIAGRAM OF THE STEELMAN 9-14-4-6W2 BRINE RECLAMATION TEST SITE, MAY 1986

CALCIUM AMENDMENT PERFORMANCE EVALUATION

Procedure. The relative abilities of gypsum and SSS to remove sodium from the soil were evaluated by comparing the salt removal performance of gypsum- and SSS-treated test zones to a control. To do this most effectively, Zones E and F were selected for comparison because they had very similar sodium concentration profiles and being beside each other, their soil composition was as similar as possible. Equivalent quantities of available calcium and nitrogen were calculated for both the amendment cases applied.

Gypsum is the traditional calcium source for reclamation because it is cheap and easily available. Saline Soil Saver is more expensive but it is a liquid which makes the calcium more readily available to the soil. It is also recognized that a liquid amendment is easier to store and apply, especially in difficult terrain. Saline Soil Saver contains nitrogen as well as calcium and so fertilizer requirements are not as high with this product as they would be with gypsum. It contains a proprietary polymeric wetting agent designed for maintaining soil spaces once the calcium has reduced the size of the clay particles. This would help prevent redispersion once reclamation has begun.

The amendments that were applied in May 1986 are presented in Table 1. The control case is represented by Zone D. The SSS-treated zone is E and the gypsum-treated one is F. Both of the amended zones were rototilled to a depth of 23 cm to improve amendment contact with the soil.

The data for this study was collected in May 1986 and October 1986. Analysis of the results was based on three key parameters: the change in soluble sodium concentration; the percent change in soil electrical conductivity (EC); and the percent change in sodium adsorption ration (SAR). These parameters reflect the removal of sodium from the soil and can be used for comparative purposes.

Results and Discussion. The May 1986 soil analysis indicated that the topsoil was 20 to 25 cm of clay loam underlain by heavy clay. Initial sodium concentrations (measured in milliequivalents/litre) in the three 20-cm layers were, from top to bottom: 318 meq/L, 252 meq/L, and 226 meq/L. The higher surface salt concentrations indicated that evaporation was taking place due to insufficient rainfall.

Results presented in Table 2 give the percent change in the key parameters that occurred between May and October 1986. The data for the control zone (D) indicate that an increase in sodium levels at the soil surface occurred during the study period and that sodium migrated from the lower soil depths. Probably, evaporation of moisture from the soil surface concentrated salts within the uppermost soil layer. Sodium levels decreased in both of the treated zones. Gypsum and SSS treatments removed equivalent amounts of salt at the soil surface but SSS has shown slightly superior performance deeper down. This is evident that because the calcium in the SSS is in a more available form it can penetrate through the soil more easily than the calcium in the gypsum.

TABLE 1 AMENDMENT APPLICATIONS USED IN THE CALCIUM AMENDMENT PERFORMANCE EVALUATION, MAY 1986

Zone	Amendment	Application Rate	Application Method
D	no additive	no additive	no additive
E	Manure	10-cm thickness	- back hoe and front-end loader
	SSS	29.5 drum/ha	- pressurized sprayer and perforated bucket
F	Manure	10-cm thickness	- backhoe and front-end loader
	Gypsum	21.5 tonne/ha	- by hand and hand-held broad caster
	Ammonium Nitrate	0.735 tonne/ha	- by hand

TABLE 2 RESULTS OF THE 1986 GYPSUM/SSS PERFORMANCE EVALUATION SHOWING PERCENT CHANGE IN KEY PARAMETERS

Zone	Soil Depth (cm)	Sodium (%)	Electrical Conductivity (%)	Sodium Adsorption Ratio (%)
Control (D)	0 to 20	18.5	13.2	1.9
	20 to 40	-42.7	-40.2	-6.5
	40 to 60	-42.6	-38.4	-2.4
SSS (E)	0 to 20	-68.4	-49.8	-58.2
	20 to 40	-27.2	-15.6	-28.0
	40 to 60	-11.5	-2.7	-20.5
Gypsum (F)	0 to 20	-64.4	-49.2	-55.3
	20 to 40	-19.7	-16.5	-16.1
	40 to 60	6.5	1.4	3.3

Flushing Assessment

Procedure. The effectiveness of flushing a calcium-amended soil was evaluated by comparing the performance of non-flushed treatment zones with identically-treated flushed ones. Flushing was carried out in July/August 1986 as well as July/August 1987.

In 1986 a total of 5.5 m^3 (75 mm of irrigation per zone) of flush water was applied in two equal treatments to the gypsum amended zone, G, and the SSS amended zones, H, I and J. Zone G was amended identically to Zone F and Zones H, I and J were amended similarly to Zone E. Water was sprayed onto the zones from a water truck. About 50% ran off the zone surfaces and even distribution was difficult to achieve.

In June 1987 a portable irrigation unit was designed and installed so that flush water runoff and distribution could be improved. A schematic diagram of the unit is given in Figure 3 and photographs of it are given in Figures 4 and 5. Runoff was reduced by providing lower flow rates than in 1986 which improved water absorption by the soil. Better distribution across the zone surfaces was also achieved by using soaker hoses to spray water evenly over each zone surface. Water flow to each hose was controlled by a valve that connected the hosing to a distribution (outlet) header. A total of 13.5 m^3 (182 mm of irrigation per zone) of flush water was supplied to four zones using this unit.

The zones flushed in 1987 were A, C, G and I. Zones A and C were ripped and will be discussed in the ripping assessment. Zones G and I were again flushed in 1987 to provide data over two growing seasons.

Results and Discussion. Results from the 1986 flushing are presented in Table 3 and may be compared to those obtained for the non-flushed case in Table 2. In general, both SSS and gypsum removed more salt when flushed. The only exception to this occured in the upper most layer of Zones I and J. These zones did not perform as well as Zone E probably because their initial salt concentrations were significantly lower than the initial Zone E levels.

Results from the 1987 flushing are presented in Table 4. By comparing the results from the non-flushed zones E and F to the flushed zones G and I it can be seen that again flushing has significantly improved salt removal rates. In fact, Zones E and F experienced an increase in sodium levels that was more extreme in the shallower depths. This is probably the result of surface evaporation bringing salts towards the surface.

It appears that flushing maintains a net downward flow of salts through the soil profile.

Ripping Assessment

Procedure. Zones A, B and C were ripped to a depth of 75 cm with a one-shank ripper mounted on a backhoe. Amendments, application rates and application methods are given in Table 5. Zone A was amended identically to Zone F and Zone B was amended in the same manner as Zone E. Zone C was amended similarly to Zone F except that straw was used instead of manure. The amount of straw used closely approximates the manure loading used on F.

Both zones A and C were flushed in 1987.

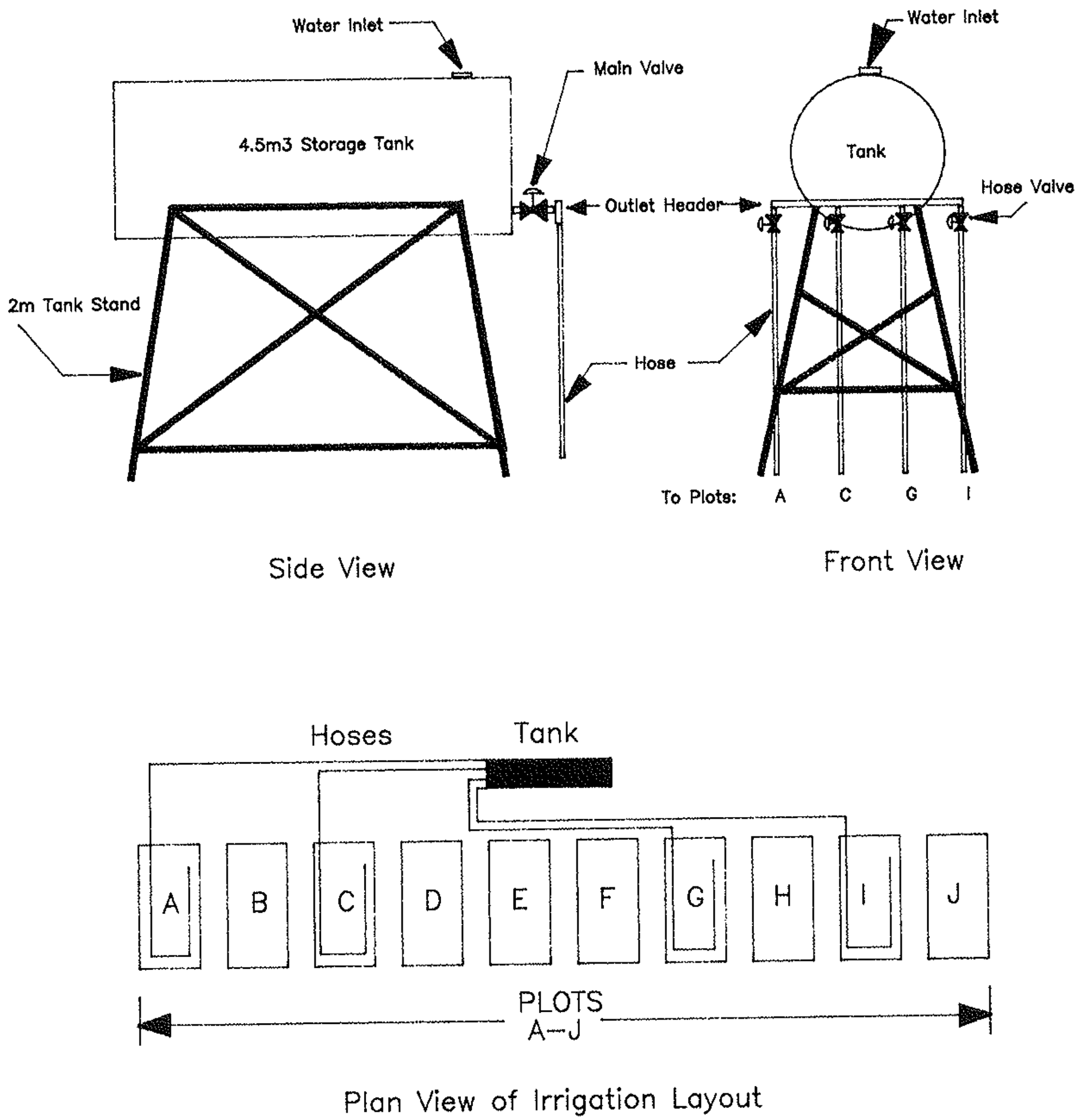


FIGURE 3 SCHEMATIC DIAGRAM OF PORTABLE IRRIGATION SYSTEM USED DURING MAY 1987 TO SEPTEMBER 1987 AT STEELMAN 9-14-4-6W2

FIGURE 4 PHOTOGRAPH SHOWING A SIDE VIEW OF PORTABLE IRRIGATION UNIT USED FOR FLUSHING PROGRAM IN 1987

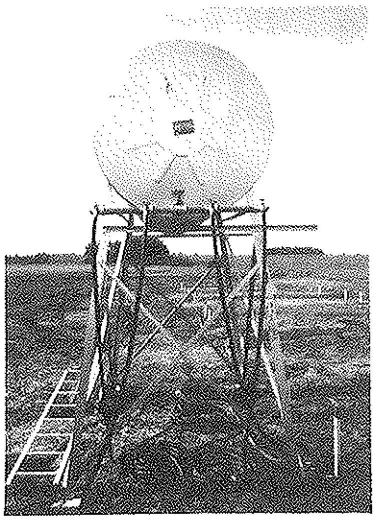


FIGURE 5 FRONT VIEW OF PORTABLE IRRIGATION UNIT SHOWING DISTRIBUTION (OUTLET) HEADER AND HOSE CONNECTIONS

TABLE 3 RESULTS OF THE 1986 FLUSHING ASSESSMENT PROGRAM SHOWING PERCENT CHANGE IN KEY PARAMETERS

Zone	Soil Depth (cm)	Sodium (%)	Electrical Conductivity (%)	Sodium Adsorption Ratio (%)
G (flushed/ gypsum)	0 to 20	-70.8	-43.9	-65.8
	20 to 40	-48.3	-18.5	-46.8
	40 to 60	-39.6	-10.0	-34.8
H (flushed/ SSS)	0 to 20	-65.5	-27.6	-57.6
	20 to 40	-58.3	-23.8	-55.1
	40 to 60	-47.3	-14.2	-45.3
I (flushed/ SSS)	0 to 20	-29.0	-46.2	-42.1
	20 to 40	-38.6	-3.7	-45.3
	40 to 60	-38.3	2.6	-43.4
J (flushed/ SSS)	0 to 20	-49.3	-18.6	-49.9
	20 to 40	-36.0	-21.9	-40.8
	40 to 60	-28.8	-18.3	-28.5

TABLE 4 RESULTS OF THE 1987 FLUSHING ASSESSMENT PROGRAM SHOWING PERCENT CHANGE IN KEY PARAMETERS

Zone	Soil Depth (cm)	Sodium (%)	Electrical Conductivity (%)	Sodium Adsorption Ratio (%)
G (flushed/ gypsum)	0 to 20	-2.8	-4.4	-8.5
	20 to 40	-4.9	-8.3	-11.3
	40 to 60	-11.2	-15.4	-19.6
I (flushed/ SSS)	0 to 20	-13.6	-41.5	-4.3
	20 to 40	-0.3	-7.7	-5.4
	40 to 60	3.2	-0.4	-6.8
F (gypsum)	0 to 20	6.6	4.4	9.0
	20 to 40	2.0	0.4	2.7
	40 to 60	3.0	-2.0	1.6
E (SSS)	0 to 20	6.1	6.1	8.3
	20 to 40	6.3	7.5	4.6
	40 to 60	-1.1	-1.7	-4.8

TABLE 5 AMENDMENT APPLICATIONS USED IN THE RIPPING ASSESSMENT

Zone	Amendment	Application Rate	Application Method
A	Manure	10-cm thickness	- backhoe and frontend loader
	Gypsum	21.5 tonne/ha	- by hand and hand-held broad caster
	Ammonium Nitrate	0.735 tonne/ha	- by hand
B	Manure	10-cm thickness	- back hoe and frontend loader
	SSS	29.5 drum/ha	- pressurized sprayer and perforated bucket
C	Straw	4 bales straw	- by hand
	Gypsum	21.5 tonne/ha	- by hand and hand-held broad caster
	Ammonium Nitrate	0.735 tonne/ha	- by hand

Results and Discussion. Soil sample results obtained in May and October 1986 were compared to evaluate:

1) Gypsum performance with and without ripping.
2) SSS performance with and without ripping.
3) Ripping performance versus flushing performance.
4) Straw performance versus manure.
5) Ripping with flushing performance.

The 1986 results are given in Table 6. Comparing this table to the results in Table 3 shows that ripping substantially improves the salt removal performance of gypsum. Because gypsum has a low solubility its penetration rate through undisturbed soil is slow. By ripping the soil, gypsum can be distributed more efficiently so that solubility is less of a problem. By comparison, ripping did not improve the salt removal performance of SSS. Since SSS is a liquid it tends to collect at the bottom of the ripped layer. This prevents an adequate calcium supply from reaching the soil that lies above.

Comparing the data for Zones G and H in Table 3 with that of Zones A and B in Table 6 indicates that flushing improves salt removal performance more than ripping does for both SSS and gypsum.

Comparing the soil sodium concentrations (Table 7) of Zone A to those of Zone C it can be determined that manure is a slightly more effective organic amendment than straw. During the dry fall, sodium left the 40- to 60-cm layer of Zone C while it accumulated in the 0- to 20-cm and 20- to 40-cm layers. The movement of salt from the lower soil layers to the upper layers is indicative of evaporation of surface moisture transporting dissolved salt upwards. During the same period, the manure-treated Zone A continued to lose salt from the shallowest depth. Therefore a downward movement of salt was maintained in Zone A during the same period. It was observed that manure formed a better surface seal than straw for reducing moisture evaporation.

Comparing the results in Table 8 with those in Table 4 indicates that ripping and flushing a gypsum-amended soil gave the highest sodium removal rates observed in 1987.

The photograph in Figure 6 shows the difference in performance for Zone D (control) and Zone C. Zone D is to the right of Zone C. It is quite bare, while Zone C has got a good vegetative cover. The foreground of the picture shows part of a farmer's field that was affected by the salt spill. Wheat seeded here failed to germinate.

TABLE 6 THE 1986 RIPPING ASSESSMENT RESULTS FOR ZONES A, B AND C SHOWING PERCENT CHANGE IN KEY PARAMETERS

Zone	Soil Depth (cm)	Sodium (%)	Electrical Conductivity (%)	Sodium Adsorption Ratio (%)
A	0 to 20	-61.8	-46.0	-52.6
	20 to 40	-43.2	-39.1	-35.2
	40 to 60	-35.1	-32.4	-16.7
B	0 to 20	-47.4	-29.3	-41.7
	20 to 40	-15.0	-36.4	-13.9
	40 to 60	-28.7	-25.2	-9.9
C	0 to 20	-77.8	-68.6	-67.9
	20 to 40	-55.7	-51.0	-35.7
	40 to 60	-38.1	-33.2	-20.2

TABLE 7 CHANGE IN SOIL SODIUM CONCENTRATION IN THE RIPPED ZONES A AND C

Sample Time	Soil Depth (cm)	Sodium Concentration (meq/L) Zone A	Zone C
May 86	0 to 20	354.67	346.00
	20 to 40	243.67	259.00
	40 to 60	197.33	199.33
Oct. 86	0 to 20	127.07	72.17
	20 to 40	138.63	114.00
	40 to 60	129.00	124.60
May 87	0 to 20	120.00	109.90
	20 to 40	139.67	134.33
	40 to 60	135.33	112.33
Sept. 87	0 to 20	26.33	22.43
	20 to 40	53.33	59.27
	40 to 60	59.40	75.03

TABLE 8 RESULTS OF THE 1987 FLUSHING OF A RIPPED SOIL SHOWING PERCENT CHANGE IN KEY PARAMETERS

Zone	Soil Depth (cm)	Sodium (%)	Electrical Conductivity (%)	Sodium Adsorption Ratio (%)
A (ripped/ flushed/ manure)	0 to 20	-27.3	-25.9	-41.5
	20 to 40	-35.5	-40.1	-44.7
	40 to 60	-38.3	-40.5	-42.0
C (ripped/ flushed/ straw)	0 to 20	-26.8	-28.6	-38.9
	20 to 40	-29.0	-30.1	-30.4
	40 to 60	-18.2	-20.5	-13.0

FIGURE 6 PHOTOGRAPH SHOWING CONTROL ZONE D FLANKED ON THE LEFT BY AMENDED ZONE C; ZONE D IS BARE WHILE ZONE C HAS GOOD COVER (May, 1987)

Conclusions

Soil salt concentrations in the control zone increased during the study period as a result of surface moisture, evaporation, and low rainfall.

The amendment program that exhibited the largest salt removal rate included gypsum, ammonium nitrate and manure applications with soil ripping and flushing during the summer. The calcium product Saline Soil Saver performed better than gypsum when neither one was aided by ripping or flushing.

Manure was considered to be a better organic amendment than straw because it afforded better protection against surface moisture evaporation.

Recommendations

The following is a recommended reclamation program for dispersed brine-contaminated agricultural soils in a semi-arid climate based upon the findings from this study and past practices.

1. Determine the degree of contamination by conducting a soil sampling program. The results of this analysis should provide a soil calcium requirement as well as nutrient demands.

2. Assess the drainage characteristics of the site, taking into account the soil texture. Install underground drainage such as weeping tile if needed.

3. Apply calcium in the form of gypsum as specified by the soil analysis. Saline Soil Saver is not recommended in most cases because gypsum with ripping and flushing has been found to perform better. Situations where it might be used would include areas with difficult terrain or when gypsum is not available.

4. Apply fertilizers such as ammonium nitrate (34-0-0) to promote revegetation.

5. Thoroughly rip the soil to approximately 75 cm to break up surface hard panning and to improve gypsum penetration.

6. Liberally apply an organic amendment, preferably well-aged manure (e.g., 10 to 15 cm thick).

7. Rototill the above treatments into soil at least 15 cm.

8. Provide some type of irrigation to maintain the downward leaching of excess salts. In areas that are distant from a water supply, tanks may be rented and filled from water trucks or, if the demand is high enough, a portable irrigation unit might be purchased to serve a number of sites at once. Irrigation rates need not be high; therefore, pumping demands can be minimized. A soaker hose design or drip style irrigation is sufficient.

References

Richards L.A. et al., Diagnosis and Improvement of Saline and Alkali Soils, U.S. Government Printing Office, Washington, D.C. (April, 1949).

Henry, J.L. and W.E. Johnson, The Nature and Management of Salt-Affected Soils in Saskatchewan, Saskatchewan Department of Agriculture (July, 1979).

de Jong E., Field Manual Information and Action Regarding Salt and Related Spills in Saskatchewan, Canadian Petroleum Association, Calgary, Alberta (1977).

Acknowledgements

This study was initiated by A.R. Teal and Esso Petroleum Company and support for the work was provided by B. Glendinning and R. Fuglerud of Esso Resources Saskatachewan Production Operations.

RESEARCH ON BOILING LIQUID EXPANDING VAPOUR EXPLOSIONS

Submitted by: C.A. McDevitt, F.R. Steward, and J.E.S. Venart
Fire Science Centre
University of New Brunswick
P.O. Box 4400, Fredericton, New Brunswick, E3B 5A3

Introduction

A BLEVE is defined as a major container failure, into two or more pieces, at a moment in time when the contained liquid is at a temperature well above its boiling point at normal atmospheric pressure (Walls, 1979). A typical example is that of a propane tank engulfed in a fire.

As the fire heats the liquefied gas, the pressure inside the container increases. The temperature of the tank metal below the liquid level does not rise much above the boiling point of the contained liquid because the heat added by the fire is removed by the boiling propane. However, the metal above the liquid level increases in temperature since heat transfer between the metal and the vapour is relatively poor. When the pressure inside the tank reaches the set pressure of the safety relief valve, the valve opens to keep the tank at this pressure. While this pressure would be safe at normal temperatures, the metal is now weakened by the high temperature caused by the fire. When the metal fails, the liquid is exposed to atmospheric pressure and is well above its boiling point. Under certain conditions this results in a violent explosion.

Once containment is lost, the liquid inside the tank boils, since it is no longer under pressure, and gives the first two letters of the phenomenon - Boiling Liquid. As the liquid boils, vapour is formed. The specific volume of the vapour is much larger than that of the liquid, so there is expansion - Expanding Vapour. There is an Explosion because there is a shock wave and the container is torn apart.

Under what conditions do tanks and their contents BLEVE? Not every pressurized liquid container BLEVEs when a tear develops in a tank. What is special about the vessels that have BLEVEd? What alterations in tank design can be made to minimize the likelihood of this type of explosion? Research is being conducted on BLEVEs with propane and Freon 12 at the Fire Science Centre of the University of New Brunswick.

BLEVE Experiments

Since a BLEVE is an explosion due to rapid boiling and expansion, there is no ignition or chemical reaction involved. In order to prove this, experiments have been done with both propane (a common fluid in large-scale, very damaging BLEVEs) and a noncombustible fluid, Freon 12 (R12). The tanks used were commercially available 1 L propane cylinders (Figure 1).

The relief valve was removed from these tanks and they were purged with nitrogen. The instrument cluster of three type "T" thermocouples and a 0 to 1000 psig Mediamate pressure transducer was inserted in the pressure relief port. The cylinders were then

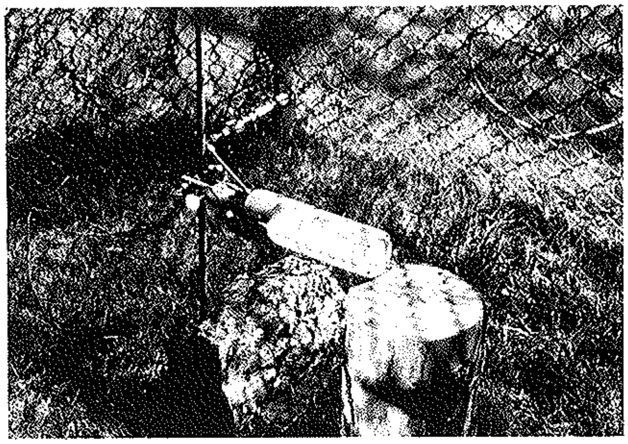


FIGURE 1 INSTRUMENTED EXPERIMENTAL TANKS

placed in a -45°C temperature bath and filled to the desired weight with propane or R12. The filled, instrumented cylinders were then ready to test.

Most experiments were carried out at the Lake George Gun Club, 40 km from Fredericton. The cylinders were mounted horizontally about 0.6 m above the ground and a propane torch was placed so that the flame would impinge on the bottom (liquid section) of the cylinder (Figure 2). This simulates a normal BLEVE situation; there is either total fire engulfment or flame impingement on the tank. The instrumentation was connected to a Hewlett-Packard 3497A Data Acquisition Unit, driven by an HP 85 computer. The computer recorded and printed temperature and pressure information. A high-speed camera was set up with a remote trigger to record the event at a maximum of 10 000 pictures per second (pps) (Figure 3). A remote digital thermometer and the camera trigger were mounted in the club house, 75 m from the cylinder. A chain link fence enclosure was placed around the cylinder to contain the pieces of the tank and to protect equipment and personnel.

A BLEVE normally occurs when the tank fails due to a structural problem produced when the metal surface overheats at a particular point. In this set of experiments it was desired to have the tank fail at a particular set of internal conditions. This failure was brought about by rupturing the tank with a .22-250 full metal jacketed bullet or a high pressure water gun provided and manned by J-Divison of the RCMP (Royal Canadian Mounted Police). This water gun shoots a 100 mL slug of water (2-cm diameter) at a maximum velocity of 189 m/s to a maximum pressure of 124 000 kPa (Figure 4), while the rifle bullet velocity is 1082 m/s.

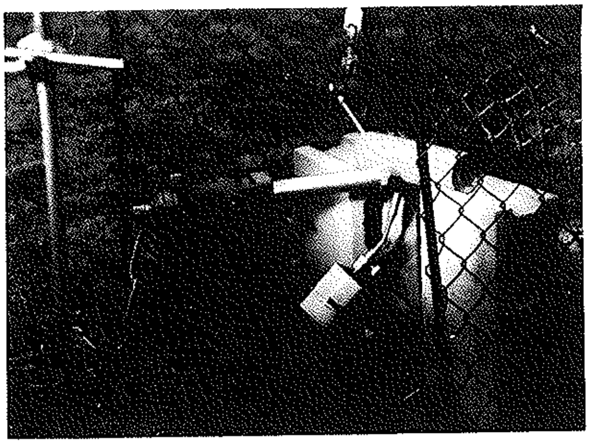


FIGURE 2 TANK WITH PROPANE TORCH AS HEATING ELEMENT

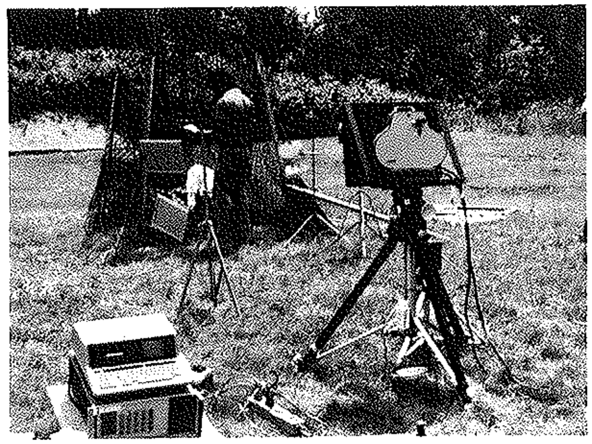


FIGURE 3 EXPERIMENTAL SETUP, TANK, COMPUTER AND CAMERA

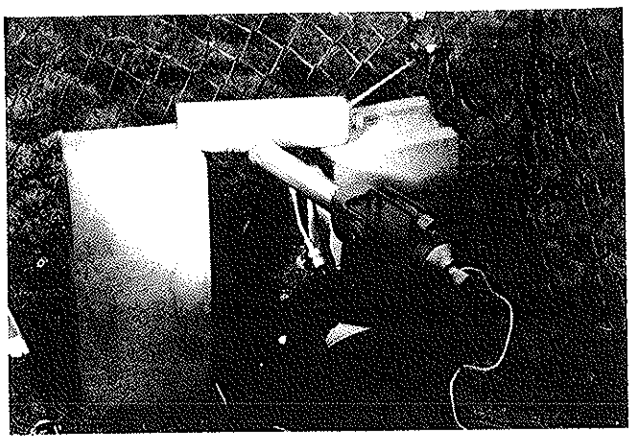


FIGURE 4 SETUP WITH WATER GUN

Once the instrumentation was connected and tested, the torch under the cylinder was lit and all personnel moved into the club house to monitor the temperature rise on the remote thermometer. When the bulk temperature reached the test value, the camera was started and the rifle fired. Results (BLEVE / no BLEVE) were recorded and the pieces photographed (Figure 5).

Before the water gun was used, it was tested on an empty cylinder and one filled with water to ensure that it could penetrate the tank wall. The cylinder wall was penetrated by the water and the water gun was then used in the same manner as the rifle.

BLEVE / no BLEVE

Results of tests conducted using 1-L cylinders filled with propane and R12 are presented in Table 1. Tests 3 to 36 are an attempt to determine the relationship between temperature and BLEVEs -- to actually test the theory that the minimum temperature below which no BLEVE can occur is the superheat temperature limit (T_{sl}). (For more

TABLE 1 BLEVE RESEARCH RESULTS

Test	Fluid	Tmin (°C)	P (kPag)	Weight (g)	H_2 (J/g)	Q (kJ)	Result
* 3	Propane	12	-	130	125.530	16.936	-
5	Propane	16	-	~138	135.957	~19.417	-
* 6	Propane	64	-	154	274.449	42.996	-
* 7	Propane	101	-	125	-	-	-
8	Propane	82	6143	501	339.373	172.403	BLEVE
11	Propane	65	2696	369	277.790	104.255	BLEVE
12	Propane	55	2200	434	245.767	108.722	BLEVE
E	Propane	35	1331	~340	187.180	~65.255	-
4	Propane	86	3930	384	356.960	138.895	BLEVE
14	Propane	73	3034	368	305.401	114.134	BLEVE
15	Propane	56	1979	332	248.866	84.199	-
16	Propane	57	2241	329	251.962	84.457	-
18	R12	73	-	1136.9	110.813	115.757	BLEVE
21	R12	39	2082	914.2	73.575	59.039	-
22	R12	71	2310	938.5	108.468	93.355	-
23	Propane	61	2613	419	264.657	112.879	BLEVE
31	Propane	58	2179	319	255.099	82.890	-
32	Propane	56	2413	340	248.866	86.228	-
33	Propane	56	2268	355	248.866	90.032	-
* 34	Propane	72	2820	252	277.790	73.167	-
35	Propane	70	3358	331	294.774	99.141	BLEVE
* 36	Propane	60	2337	323	261.468	85.987	-
41	Propane	50	-	430	230.349	101.090	BLEVE
* 42	Propane	52.6	-	424	239.715	103.651	-
43	Propane	65	-	448	277.790	126.576	BLEVE
44	R12	66	-	1082	102.614	101.296	BLEVE
45	R12	67	3744	1133	103.761	107.030	BLEVE
46	R12	67	3013	1112	103.761	105.380	BLEVE
47	R12	59	2082	1131	94.650	96.876	BLEVE

Where:

Q = the amount of heat measured in kJ that would be released when the liquid changes from its pressurized condition in the tank to saturated liquid at atmospheric pressure (Osigo, 1972). Q is calculated from the equation:

$$Q = g\,(H_2 - H_0)$$

g = the weight of the fluid in grams.

H_2 = the liquid enthalpy of the fluid at the time of rupture, measured in J/g

H_0 = the enthalpy of the saturated liquid at its normal boiling point, measured in J/g.

H values are from ASHRAE Handbook, 1981 Fundamentals (Basis: $H_0 = 0$ for saturated liquid propane at -45°C, saturated liquid R12 at -40°C)

* Only one thermocouple working, may be vapour temperature

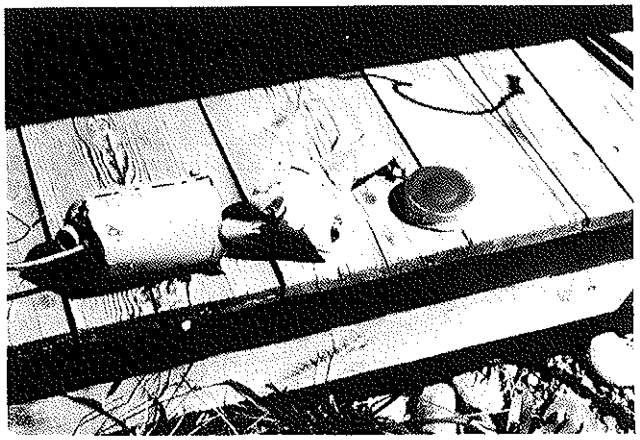


FIGURE 5 CYLINDER WHICH HAS BLEVEd

information on this theory, see McDevitt et al., 1987). This temperature is 53°C for propane and 69°C for R12.

Cylinders were heated to a specific temperature and then ruptured to observe if a BLEVE would occur below the T_{sl}. Not all cylinders used for these tests contained the same weight of liquid. Results showed that one factor which determines whether a tank BLEVEs is the amount of liquid in the cylinder. For example, Tank 12 containing 434 g of propane BLEVEd at 55°C; Tank 16, filled with only 329 g did not explode at 57°C, nor did Tank 34 at 65°C (252 g propane). Tanks 16 and 34 were above T_{sl}, and would have BLEVEd if that were the only criterion. Temperature, therefore, is not the only important parameter for determining the possibilty of a BLEVE. The quantity Q is the heat initially available to vapourize the fluid; therefore, Q is a measure of the amount of vapour that could be formed. No cylinders BLEVEd below a Q of 96.7 kJ, while all of the tanks with a Q above this value did BLEVE.

The next series, numbers 41 - 47, attempt to test the possiblity that the occurrence of a BLEVE depends on the amount of vapour that could be produced when the tank was ruptured. With the minimum Q now determined, results could be predicted. Calculations based on the minimum Q of 96.7 kJ show that a cylinder should BLEVE at 50°C if it contains at least 427 g of propane and at 65°C with at least 1077 g R12. Both of these temperatures are below the stated T_{sl}. If these tanks explode then BLEVEs can occur below the T_{sl} temperature. Cylinder 41 was filled with 430 g of propane and burst at 50°C - it BLEVEd, as predicted. Tank 44 which had an R12 loading of 1082 g also BLEVEd at 66°C; below its T_{sl}.

Tanks 45, 46 and 47 were filled with 1133, 1112, and 1131 g of R12, respectively. All of these tanks were predicted to BLEVE at 65°C or higher. The water gun was used by the RCMP to rupture these cylinders.

Tank 46 was burst at 67°C and BLEVEd. The gun was aimed at the liquid space, as in most of the previous tests. To determine if rupture location had any bearing on the results, the gun was suspended above the cylinders and aimed at the top (vapour space) for the next two tests. Both of these tanks BLEVEd, tank 45 at 67°C and tank 47 at 59°C.

The temperatures quoted are bulk liquid temperatures, measured near the bottom of the tank. There is some stratification in the liquid, and the vapour temperature is also higher than the liquid temperature. Typically the spread in propane tanks is 2°C to a maximum of 6°C and 11°C for R12 tanks. Because these cylinders are more than 90% liquid full at rupture conditions, the vapour temperature is not significant. For test 47 the liquid bulk temperature was 59°C and the vapour temperature was 68°C. Thus all temperatures in the vessel were below the T_{sl} of 69°C. Based on these tests, it is possible to have a BLEVE below T_{sl}. The superheat temperature limit, therefore, cannot be used to predict a BLEVE.

To ensure that the temperature measurement was accurate, all of the thermocouples in the last three tests were calibrated at room temperature and in boiling water and shown to be accurate to $\pm$0.3°C. To check response time, the thermocouples were heated with a match and immersed in cold water while temperature vs time was recorded. The plots showed that the thermocouples responded much faster than the temperature of the fluid in the cylinders changed during the tests.

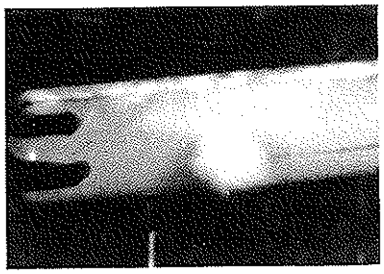
Discussion

Follow the progression of a BLEVE in the high speed photographs in Figures 6 and 7. First the bullet passes through the cylinder (a), making the same size hole on both entry and exit. There is tearing from the exit hole longitudinally until the tear encounters the welded, double metal of the centre and bottom seams. Then the tears progress circumferentially in both directions, opening up and flattening out the lower section of the cylinder (b). As the tears progress to the front of the tank, the ends of the cylinders begin to move away from each other (c). The bottom half of the tank becomes completely separated from the top, the top half moves to the right, the bottom to the left and the flattened piece is projected toward the camera (d). Note that Figure 6 is a propane BLEVE and Figure 7 has R12 as the contained fluid. The mechanism and results are identical in both cases.

Parameters. Logically, it takes a certain amount of energy released to produce the type of damage seen in the figures. If this much energy is not available, then the tank will not BLEVE. Q, a measure of the amount of vapour produced, is also a measure of the destructive energy available. For these particular cylinders, assuming constant conversion of energy to destructive work, Q must be above 96.7 kJ. If the cylinder were of a different metal, with different yield stress, then the required Q could be different. This assumes that it is the vaporization process that is driving the explosion.

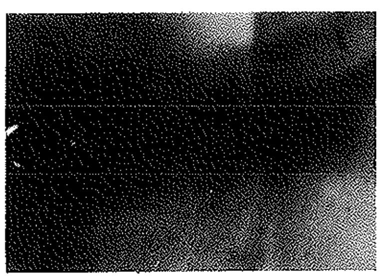
Waves. Another previously unmentioned phenomenon, which may play a role in the BLEVE process, is that of sonic pressure waves. When the hole is made in the tank, the surrounding liquid is exposed to atmospheric pressure. This new pressure information must be transmitted to the rest of the liquid. Therefore there must be a rarefaction wave which travels at the speed of sound in the liquid. Just behind this wave will be boiling liquid, which will cause pressurization, thus a pressure wave will follow the rarefaction wave. The pressure wave may be slower because it is not travelling through a homogenous liquid, but through a two-phase mixture. It is also travelling through a lower pressure liquid. These two waves have not as yet been seen or measured, but they may have some effect on the events during the explosion.

a) at rupture



b) after 1 ms

c) after 1.5 ms



d) after 2 ms

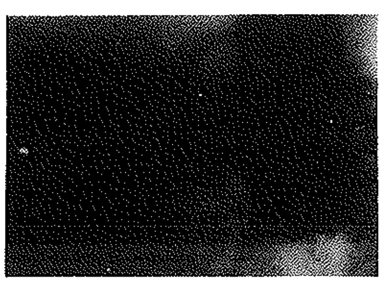
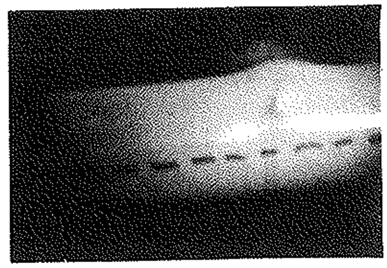
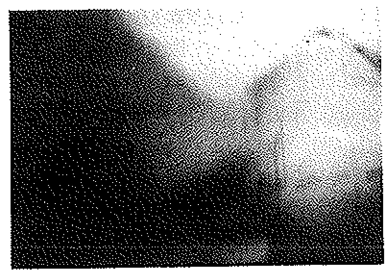


FIGURE 6 PROPANE BLEVE AT 73°C

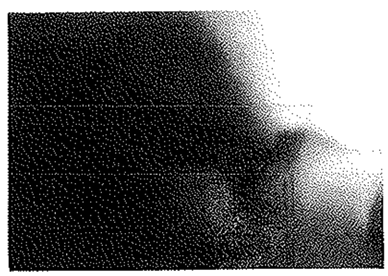
a) at rupture



b) after 1.25 ms



c) after 2.5 ms



d) after 2.75 ms

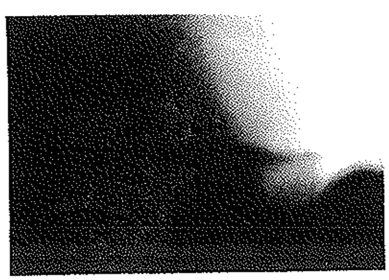


FIGURE 7 R12 BLEVE AT 73°C

Fireballs. Finally, the issue of the fireball. When a propane tank BLEVEs, it leaves a large propane vapour cloud. If there is some source of ignition, usually the fire which caused the BLEVE, then this cloud can ignite and a fireball may form. Depending on the amount of the flammable material released, these fireballs can reach a hundred metres in diameter and are quite spectacular. Also, damage from the thermal radiation of the fireball is worse than the damage caused by the overpressure of the BLEVE. Most papers published from the scientific community recognize that the BLEVE and the fireball are two separate events. There is overpressure associated with a BLEVE, and none with a fireball. The connection between a BLEVE and the fireball is that the BLEVE provides the fuel for the fireball. The BLEVE, however, has occurred long before the fireball is formed.

There are some authors in industry who suggest that the definition of a BLEVE be changed to include the fireball. They suggest that if there is no fireball, there is no explosion (Lewis, 1985; Ens, 1985). Our research has shown that the two events are most definitely separate, one occurring much later than the other. Results show the explosion and 260 ms later, after all of the fragments of the container are beyond the field of view of the camera, the ignition of the vapour and a fireball. In fact most of our BLEVEs, even with propane, had no fireball as there was no source of ignition. It is important for firefighters, loss prevention, and risk analysis personnel to recognize the BLEVE potential even when dealing with inert pressure liquefied gases.

Theories

Detonation. There are some similarities between a boiling liquid expanding vapour explosion and a detonation (chemical reaction-driven explosion). The most obvious is that they are both explosions, i.e., both produce overpressures and make a loud noise (the wave is supersonic). It is possible that the similarities go further.

Detonation is in itself a process in which there is much uncertainty and much research; however, a rough description of how a detonation proceeds is described as follows:

> A shock wave propagating into undisturbed explosive material instantaneously compresses and heats it enough to initiate chemical reactions that, over the course of several nanoseconds, release energy. The energy in turn preserves the conditions of high pressure and temperature necessary to drive the shock wave forward. When the reactions have run to completion at the end of the reaction zone, the gases expand to do work (Davis, 1987).

The shock wave in a BLEVE would be the rarefaction wave carrying the new pressure information to the liquid, at sonic velocity. In its wake will be a pressure wave due to the boiling of the liquid as it moves toward a lower pressure zone. This wave may be slower and broader because it is travelling through a two-phase mixture and the speed of sound in vapour and in the lower pressure liquid is much slower. There would be pressurization due to the limited volume. The gas expansion does work; the work of tearing the cylinder.

A possible scenario which fits the observations that have been made to date is as follows: The cylinder is partially opened by the bullet and the rarefaction wave begins at the hole and travels toward the ends of the tank. In its wake it leaves boiling liquid. This liquid cannot continue to boil because as the pressure is raised (due to vaporization), boiling will stop. There will be bubble collapse in this region, which is known to cause large pressure rises (Dake, 1983). This starts to tear the centre section of the tank. As the rarefaction wave hits the ends of the cylinders, a large ΔP occurs which causes the ends of the tank to move away from each other. The centre section is already torn open, and the movement of the end sections continues this tearing. Boiling will start at the end sections, giving the rocketing effect, but there is no damage here as there is no bubble collapse. (There is nothing to sustain pressure on the liquid as the container is now fully open to the atmosphere).

Future Work. There must be rarefaction and pressure waves propagating through the liquid, but these have not as yet been measured. It may be that the pressurization due to the boiling is causing the explosion, as mentioned previously. There also will be bubble collapse associated with this pressurization, and that occurrence is also known to produce large overpressures. The next step in this research is therefore to try and see what is going on inside the cylinder just as there is a tear.

This will probably be done in a typical shock tube, modified so that there are blow-out sections and a section that can easily be punctured. High-speed photography will hopefully show the boiling, and rapid recording instrumentation will mark the wave travel. This type of experiment, along with a view inside the test section, may improve our understanding of the initiation of a BLEVE.

Conclusions

The superheat temperature limit cannot be used to predict BLEVEs. It has been shown that BLEVEs can occur below this temperature. There appears to be a relationship between liquid temperature, liquid volume, and the energy required to drive the BLEVE. It was found that Q must be above 96.7 kJ for the experiments conducted with 1-L commercial propane cylinders.

Fireballs may occur after a BLEVE of flammable material. They are not part of the tank destruction. There can be a BLEVE without a fireball just as there can be fireballs without any boiling liquid.

Experiments should be conducted in a windowed shock tube. These experiments should give information concerning the mechanisms inside the tank.

Rupture location (vapour vs. liquid space) appears to have no effect on whether a container will BLEVE.

Acknowledgements

The authors would like to express their thanks to J-Division of the RCMP, and in particular Special Constable H. Gould, for their cooperation and assistance.

Funding for this work has been provided by Transport Canada, The Transportation Development Centre, and the National Science and Engineering Research Council of Canada Strategic and Operating Grant Programs.

Rifle range facilities were kindly provided by the Lake George Gun Club. Professor J. Mersereau provided the precise marksmanship necessary for the experiments. Mr. O. Scott was the technical expert for the high speed filming.

References

Davis, W.C., "The Detonation of Explosives", Scientific American (May, 1987).

Dake, J.M.K., Essentials of Engineering Hydraulics, MacMillan press, London (1983).

Ens, H., "Letters to the Editor", Hazardous Cargo, 6, 9, p. 65 (1985).

Lewis, D., "New Definition for BLEVEs", Hazardous Cargo, 6, 4, p. 28 (1985).

McDevitt, C.A., et al., "What is a BLEVE?", Proceedings of the 4th Technical Seminar on Chemical Spills (Feb., 1987).

Ogiso, C. et al., "On the Mechanism of Vapour Explosion", PACHEC (1972).

Walls, W.L., "The BLEVE - Part 1", Fire Command, p. 24 (May, 1979).