DEFENCE RESEARCH ESTABLISHMENT SUFFIELD
RALSTON ALBERTA

SUFFIELD SPECIAL PUBLICATION 65

SUMMARY REPORT ON SYSTEMS FOR THE DISPOSAL OF MUSTARD STOCKS AT DRES

by

C.R. Iverson

July 1973

TABLE OF CONTENTS

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INTRODUCTION

Since World War II, about 737 tons of Mustard (a chemical warfare agent) has been held in storage at the Defence Research Establishment Suffield (DRES). For many years, the Canadian Government and the Department of National Defence have had no foreseeable need for, nor interest in retaining, this now obsolete stockpile of chemical agent. Although Canadian Government policy stipulates that the Canadian Forces shall retain a capability to protect themselves against a chemical attack, the policy is equally clear that the Canadian Forces shall neither retain, nor acquire, a capability to undertake offensive operations involving the use of chemical warfare weapons. In compliance with this policy, the Canadian Forces have no bombs or ammunition in their inventory which are designed, or capable of being used, for the dissemination of chemical warfare agents.

The Canadian Government (through External Affairs with some DRB scientific assistance) has actively supported at conferences in Geneva, the concept of some form of international agreement to prevent the future use of chemical warfare techniques. To this end, it has been recognized for some time that the credibility of the Canadian Government position may not be complete until its last remaining stockpile of the World War II chemical warfare agent has been destroyed. Further, although the mustard at DRES is safely stored, it is recognized that it will not be practical to continue to store the material until such a time in the very distant future when natural decomposition renders the material non-hazardous. For these reasons, and others, it was decided in early 1972 that DRES should undertake applied research and engineering studies aimed at leading to a safe and practical method for disposal of mustard.

MUSTARD IN STORAGE AT DRES

During World War II, quantities of mustard were manufactured in Canada and shipped to Suffield, Alberta for storage. A total of ten reinforced concrete, lead lined vaults were constructed for storage purposes. These vaults have inside dimensions of 35 feet by 20 feet and are 12 feet in height. They are about one-half below ground level and each has circular access ports on the top. Mustard was only stored in four of these. Of the remaining vaults, two remain empty and four have been modified and used for temporary storage of radioactive wastes, storage of documents and for laboratories. The contents of the vaults containing mustard are as follows:

Vault Identification No.	Type of Mustard	Approx. Weight of Mustard (tons)	Approx. Height of Mustard (feet)
6	HT	117	3
8	HS	200	6
9	HS	210	6½
10	HS	210	6½
	Totals	737	22

The above tonnage figures are based on inventory records. A detailed analysis of the viscosity, density, heat content, filtration properties and chromatograms for samples taken from various levels within each vault has been carried out and documented in the references to this report and in other internal DRES documentation.

ENVIRONMENTAL CONSIDERATIONS

As evidenced by the recently completed program on the disposal of Canadian stocks of DDT and in keeping with Canadian Government policy, the Defence Research Establishment Suffield has for years maintained a high regard for protection of the environment in all of its experiments, trials and operations. Although safety of operation must be given a high priority in selecting a process to be used for disposal of highly toxic materials, environmental cleanliness and costs must also receive their appropriate consideration. Also, as part of the general instructions from our Defence Research Board Headquarters, we were directed to aim for a high degree of environmental cleanliness in planning a system for disposal of mustard.

Since in many cases we were "breaking new ground" in the application of technology, we were frequently in the first instance concerned in the main with establishing the scientific validity of any process under consideration. This work was then followed by applied research and engineering studies leading to a system and procedures which would result in a high rating of environmental acceptability. On environmental matters we have solicited and are obtaining assistance from Environment Canada, the Alberta Government Department of Environment, the Research Council of Alberta, Western Research and Development Ltd. of Calgary and consultants from the universities of Alberta and Waterloo.

MAJOR SYSTEM CONCEPTS AND PROCESSES STUDIES

Although a large number of concepts for disposal of the mustard were considered to various degrees of detail, four of these received in depth scientific and engineering study as being viable contenders on which a decision could be made concerning:

- Should a mustard disposal program be undertaken at this time or should one await the advancement of technology or better ideas for disposal?
- If a disposal program is to be undertaken, which process should be selected and what are the estimated costs and time schedules?

The four system concepts and processes studied in detail were:

- Thermal Destruction using a high temperature furnace and scrubbers for removal of the HCl and SO_2 Effluents (similar to U.S.A. process)
- Thermal Destruction using a high temperature furnace and a high temperature, corrosive resistant smokestack for distribution of the effluents.
- Chemical process based on hydrolysis to produce water soluble liquid waste products of reaction.
- Chemical process using sodium sulphide to produce insoluble solid waste products of reaction.

Details of these processes and the results of related scientific and engineering investigations are reported in the various references to this document and a summary only of the various system concepts and processes is given below.

THERMAL DESTRUCTION WITH SCRUBBERS

As a consequence of the experience acquired and success in disposal of DDT by thermal destruction, it was decided to examine the feasibility of using high temperature methods for complete breakdown of the molecular structure of mustard. These techniques were being used successfully in similar operations in the U.S.A. and the U.K. for disposal of mustard. Theoretical combustion studies also confirmed the validity of the process. The breakdown products of combustion of pure mustard are H_2O, CO_2, HCl and SO_2 assuming adequate temperatures and dwell times are provided by the furnace.

Studies confirmed that a high temperature furnace of the type used by DRES for DDT destruction would be suitable and could operate at a burn rate of about 8 tons per 24 hour day using a mustard to natural gas ratio by weight of 3.25 to 1 as used at Rocky Mountain Arsenals. This would involve a total natural gas consumption of about 10 million cubic feet for destruction of the entire mustard stocks. However, the other system components would limit the burn rate to about 5 tons per 24 hour day which would require a total of about 24 million cubic feet of natural gas to maintain a burn temperature of about 1650 degrees F. (total heat flow required is about 10,000,000 BTU/hour). The above natural gas flow rates are readily available at Suffield.

The thermal destruction process for the entire mustard stocks would produce an estimated 310 tons of HCl gas with a production rate of 190 pounds of HCl per hour based on a 5 ton/24 hour day mustard burning rate. An HCl scrubber of the type now used for the HCl removal from the DDT facility at DRES would be adequate for these HCl production rates provided a larger water pump is installed.

Calcium Hydroxide would be used to neutralize the acid produced and a total of about 320 tons would be required for actual neutralization. Because of the concept of operations, some additional $Ca(OH)_2$ would be needed representing a total cost of about $10,000 F.O.B. Suffield. About 470 tons of Calcium Chloride would be produced by the reaction.

The total thermal destruction process would involve the production of about 275 tons of SO_2 with an SO_2 production rate of about 170 pounds per hour assuming a mustard burning rate of 5 tons/24 hour day. If one wishes to remove essentially all of the SO_2 then a scrubbing tower represents the most cost/effective solution for the quantities involved. A number of chemicals were considered as an agent for removal of the SO_2 with the decision (based on the manufacturer's recommendation) that soda ash (Na_2CO_3) was the best compromise.

$$Na_2CO_3 + SO_2 + H_2O \rightarrow \underset{\text{baking soda}}{NaHCO_3} + \underset{\text{sodium bisulphite}}{NaHSO_3}$$

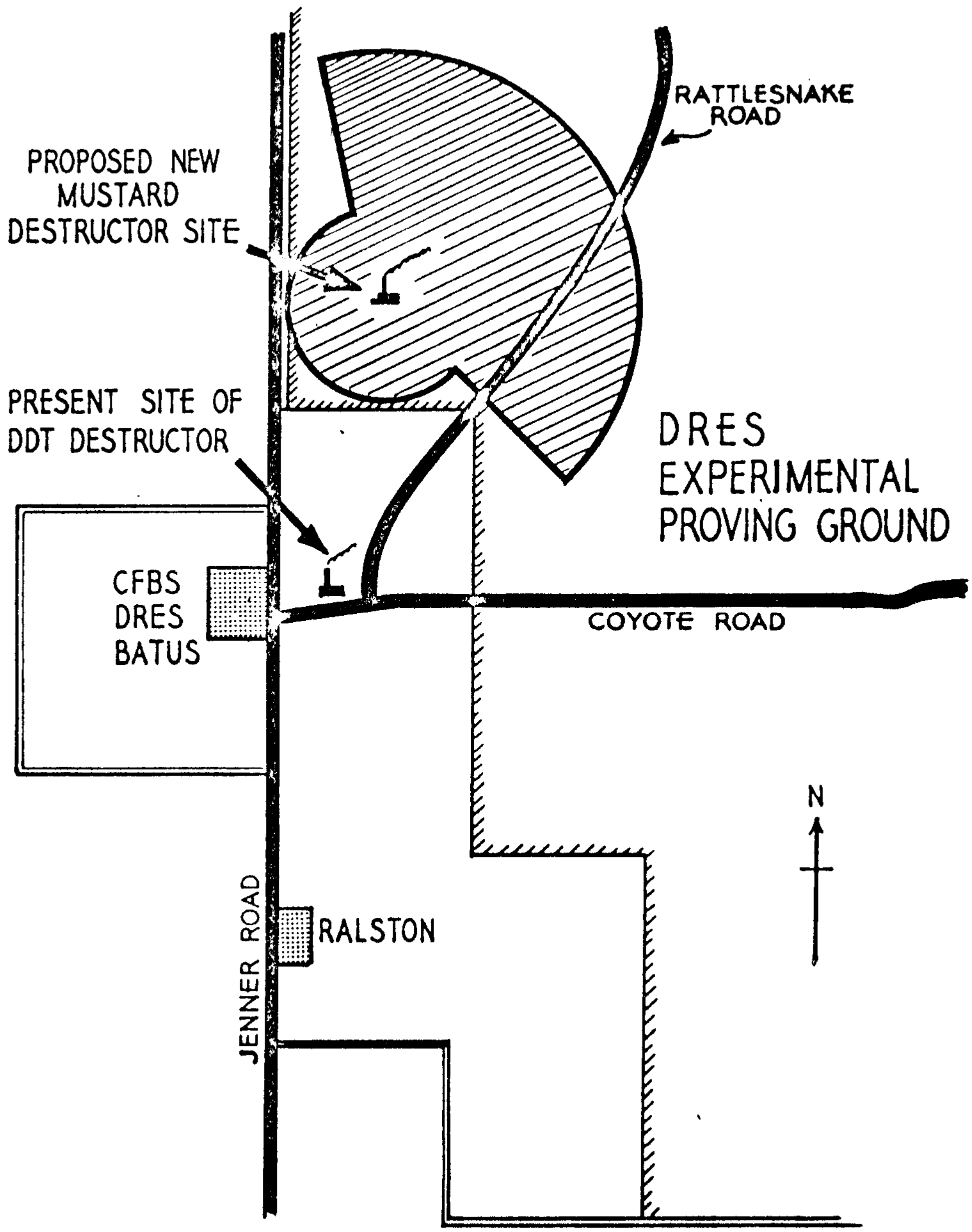
The recommended procedure is to use a 10-15% solution of Na_2CO_3 in water and to operate the system until a 1% solution results. This must then be flushed out and the process repeated. This procedure would require about \$40,000 worth of Na_2CO_3 (about 510 tons at about \$75 per ton F.O.B. Suffield). A total of about 360 tons of baking soda and 450 tons of sodium bisulphite would be produced.

During the earlier studies on thermal destruction it was assumed that these salts (470 tons of $CaCl_2$, 360 tons of $NaHCO_3$ and 490 tons of $NaHSO_3$) could be left in the corresponding water cooling ponds on the prairie adjacent to the destructor and scrubber installation. This simple concept of operations may be questioned on environmental grounds. At the mustard disposal installation in the U.S.A., a somewhat similar scrubbing process is used but they have also installed a large dryer facility to recover the salts as solids until disposal action of these salts is decided upon.

A complete system based on the above concept is estimated to cost \$380,000 plus an estimated \$60,000 in direct labour costs for a total of \$440,000. These figures assume that the existing high temperature furnace and HCl scrubber would be used but would be re-located to a satisfactory location for mustard disposal. The addition of a dryer for dealing with the salts if this were deemed necessary would result in a total cost of about \$500,000.

THERMAL DESTRUCTION WITH SMOKESTACK

This concept involves the use of a high temperature furnace as discussed above but uses a high temperature,corrosive resistant smokestack to deal with the effluents. The destructor and smokestack would be situated about 1½ miles north and ½ mile east of the administrative area of the base as shown on the map below.



The concept of operations would be to manually control the burning rate from zero to a maximum of 8 tons of mustard per 24 hour day based on data from atmospheric pollution monitoring stations and on the meteorological conditions. The burning rate would be chosen such that within the cross-hatched zone on the above map, the ground level contamination would NOT exceed the Alberta 24 hour Standard of 0.06 parts per million. The burning rate would be further reduced, if necessary to ensure that at all points outside the cross-hatched zone, the atmospheric contamination would NOT exceed the 1 year Maximum Desirable Levels of 0.01 parts per million as set forth in both the annual Arithmetic Mean Alberta Standards and in the National Air Quality Objectives for SO_2 as issued by Environment Canada as Regulations under Canada's Clean Air Act. A total of 271 tons of HCl and 408 tons of SO_2 would be discharged into the atmosphere for the entire mustard disposal program based on this system concept.

The cost for such a facility is estimated at $235,000 and labour costs are estimated at $50,000 for a total project cost of $285,000. These costs assume procurement of a new furnace and smokestack. A saving of about $40,000 could be realized if one gambles on the assumption that the present furnace could be re-located without damage to the furnace lining. A further saving could be effected if a suitable, used smokestack could be obtained.

HYDROLYSIS PROCESS

It has been known for many years that water will hydrolyse mustard and break it down into thiodiglycol and HCl. In solution the reaction is rapid, however no data were available on the rate of the heterogeneous reaction, i.e. reaction in which mustard is at a concentration which is sufficient to exceed its solubility in water. It was decided, therefore, to investigate this reaction in detail. A most significant result of this work was the discovery that the time required for the hydrolysis process to go to completion was very short provided efficient stirring, alkaline conditions and elevated temperatures were maintained throughout the course of the reaction. It then became evident that disposal by hydrolysis for large quantities of mustard would be an extremely cost effective process.

Either CaO or $Ca(OH)_2$ may be used to neutralize the HCl and maintain a near neutral mixture. Heat is produced by both the CaO and water reaction as well as in the $Ca(OH)_2$ and HCl reaction. By controlling ratios of CaO and $Ca(OH)_2$ and their addition rates it is possible to directly control both the pH of the mixture as well as its temperature.

If low ratios of water to mustard (e.g. 2:1 or 1:1) are used, then more of the mustard reacts with the thiodiglycol to produce a variety of sulphonium salts. Higher ratios of water to mustard (e.g. 4:1 or greater) results in lesser quantities of sulphonium salts and both the temperature and pH value of the mixture are more easily controlled. Gas chromatographic analyses established categorically that all of the mustard is destroyed.

Numerous laboratory and field trials were carried out to determine the rate at which a given quantity of mustard could be hydrolysed and to determine the composition and nature of the reaction products. This was done for water/mustard ratios from as high as 300:1 down to 1:1, for various temperatures from $20^{\circ}C$ up to $90^{\circ}C$, for both HS and HT, for various pH values from 2 to 14 and for several methods of stirring. A number of the tests were done in the laboratory using batch quantities of mustard from about 0.01 pounds up to quantities of about 1 pound. To confirm that there were no unforeseen scaling problems,larger trials were done in the field using quantities of mustard ranging from about 1 pound to 1,500 pounds at a batch. In total, several thousand pounds of mustard have been successfully hydrolized during these experimental tests of the process. As a consequence, a high degree of confidence concerning both the scientific and engineering feasibility of the process has been established.

Other supporting studies were related to the temperature increase of the mixture for various parameters including addition rates of both CaO and $Ca(OH)_2$, efficiency of stirring for a mustard vault shaped container and for cylindrical containers as well as studies related to corrosion problems of pumps, containers, pipes, etc., for both mustard and the products of reaction.

Once the hydrolysis process appeared to offer the lowest cost as well as the simplest and safest method for breakdown of the mustard into relatively non-vesicant and non-hazardous products, it became crucial to the study to determine whether or not an environmentally acceptable procedure could be evolved to deal with the waste products of the reaction. Numerous methods were considered and a number of supporting investigations were carried out. These related to determining the physical and chemical properties of the waste product and whether or not biodegradation takes place. Further studies were concerned with the effect of the waste products on vegetation and animal life and determination of the infiltration rates in soil. It became apparent that there were two main options. One was to spread the waste products over a very large area (e.g. several square miles) and depend on dilution with the earth and biodegradation. The other concept was to attempt to achieve near total containment in a small area (e.g. one acre of land or less).

Biodegradation does take place for the specific waste products but only slowly. Extensive tests would be needed to establish the characteristics and toxicity of the by-products of biodegradation as well as to determine the effects on the biodegradation process with penetration into the earth. It became apparent that in any reasonable period of time it would not be possible to establish a strong scientific base to defend the environmental acceptability of a concept which depends on biodegradation. For this reason, emphasis was given to studying the concept of near total containment of the waste products of the hydrolysis process.

Fortunately, for other purposes related to selecting a radioactive waste disposal site, an extensive hydrologic and geologic study had been carried out by the Research Council of Alberta on portions of the DRES Experimental Proving Ground. This separate study had located and extensively studied a particular site that seemed to offer excellent properties from containment considerations. Further, infiltration studies had indicated that even coarse sand was effective in retaining the water insoluble components of the reaction.

The concept of disposing of the waste products by land fill disposal methods at this carefully selected and proven waste disposal site appeared to provide an attractive solution to the problem. Earth containment studies using actual waste products of reaction are being carried out at the selected site with seemingly encouraging results. At this stage, we of DRES are reasonably convinced that disposal of the waste products in an acceptable manner could be effected at the particular disposal site. To further enhance the environmental acceptability of the concept it is recognized that much or all of the water could be driven off and perhaps some of the thiodiglycol; if this is deemed warranted. Further one could package the semi-dry waste products into large heavy gauge polyethylene bags and could provide total protection of the buried waste products from moisture penetration from above. These latter mentioned procedures would only have a limited life span but may be of some benefit. Chemicals, etc., could be added to the waste products to further ensure containment.

The hydrolysis concept of operations lends itself to be separated into two phases; the first being destruction of the mustard and storing, on an interim basis only, the waste products into an empty vault which is available. The second phase (and largely concurrent) would be the disposal of the waste products.

It is proposed to defer making any recommendation at this time on the second phase until time has allowed consultation with environmental experts. A seminar to discuss this subject has been arranged for 24 and 25 July 1973 with representatives from Environment Canada, the Government of Alberta Department of the Environment, the Research Council of Alberta and consultants from the Universities of Alberta and Waterloo.

The estimated costs for the phase I program only are $20,000 for equipment and material and about $20,000 for labour for a total phase I cost of about $40,000. The phase II cost cannot be determined until the total concept has been better defined but is expected to be less than the phase I costs.

SODIUM SULPHIDE PROCESS

Because of earlier uncertainties of being able to evolve an environmentally acceptable disposal plan for the waste products of hydrolysis, it was decided to search for a chemical process which would yield a non-hazardous, insoluble solid product as the main waste product of the reaction. It was deemed that such wastes could readily be disposed of by normal land fill methods.

This study led to a concept of mixing mustard with a solution of water and sodium sulphide; again with stirring and heating of the mixture to speed up the reaction. The scientific validity of the process has been firmly established by both small scale laboratory tests and large scale trials in the field. However, problems remain which were not fully solved before this study was terminated. Specifically, the whole mixing process must be carefully understood, designed and engineered to prevent the trapping of unreacted mustard within the solids being formed. Also, some engineering design effort would be required to evolve a suitable system for removing the solids from the mixing tank and for subsequent handling. Monitoring to ensure that quantities of mustard had not been trapped would also be needed before disposal of the solid with consequent engineering problems to ensure a high degree of safety for the operators.

The costs of the chemical alone using the sodium sulphide process would be about $135,000 as compared to under $10,000 for the hydrolysis process. Because of the obvious advantages of the hydrolysis process and since we are confident that a suitable disposal plan for dealing with the waste products can be evolved, we have terminated further engineering studies of the sodium sulphide process.

RECOMMENDED DISPOSAL PROCESS - HYDROLYSIS

For the following very practical and significant reasons, DRES strongly favours disposal of mustard by the hydrolysis process over all other disposal processes considered.

- Very high degree of certainty of destruction of the mustard.
- Easy and early availability of all elements and components of the necessary facility.
- No significant engineering design risks (note that near full scale experiments have been successfully carried out).
- No major facility maintenance problem can occur since if a system component requires maintenance and cannot be safely and readily decontaminated as needed for safe maintenance, the system component may be replaced in a timely manner and at modest cost.
- Operating procedures are relatively simple and all functions and processes which involve highly toxic materials and other hazards can be done unattended within the fenced enclosure area using simple remote control systems with no human operators being subjected to significant hazards.
- The proposed disposal system and procedures are relatively safe compared to all other processes and the need for operators to work in areas where full protective clothing is needed is minimized.
- The facility, material and labour costs are much lower than for all other disposal processes considered.
- The uncertainties in both scheduling and in total duration of a disposal program are less than for any other process.
- We are confident that an environmentally acceptable method can be evolved for disposal of the waste products from the process.

Note: A seminar is to be held at DRES on 24-25 July 1973 to discuss the environmental acceptability of waste disposal plans with experts from:

- Environment Canada (Ottawa and Edmonton)
- Government of Alberta, Department of the Environment
- Research Council of Alberta
- Consultants from Universities of Alberta and Waterloo.

A report on this seminar will be provided separately.

RECOMMENDATIONS

The following recommendations are made:

1. DRES undertake at earliest possible date a mustard disposal program based on the proven hydrolysis process.
2. The program be carried out in two, relatively independent but concurrent phases as follows:

   Phase I - Destruction of mustard by hydrolysis with interim storage of the waste products in empty Vault No. 7.

   Phase II - Disposal of waste products of reaction by a subsequently approved method.
3. Authority to proceed with Phase I be given at an early date to enable a good start and proving out the complete processes involved in both Phase I and Phase II during fall of 1973 with completion of Phase I before end September 1974 and Phase II before end October 1974.

Note: The above recommendations assume that as a result of the environmental seminar to be held at DRES on 24-25 July 1973, DRES confirm that a practical and acceptable waste disposal plan for Phase II can, and will, be evolved and submitted to DRB/HQ for approval.

REFERENCES

1. "Status Report on Studies for Disposal of Mustard" by C.R. Iverson - Annex A to DRES 170-80/S87 (DG) dated June 73.

2. "Summary Report on the Thermal Destruction of Mustard" by C.R. Iverson, 12 Sep 72

3. Complementary Investigations at DRES Related to the Thermal Destruction of Mustard" by S.B. Mellsen, Suffield Technical Paper No. 409, Apr. 73.

4. "A Preliminary Engineering Feasibility Study on Methods of Thermal Destruction of Mustard" prepared by Western Research & Development Ltd., Calgary, Alberta, 15 Sep 72 (Contract to DRES)

5. "Study of Mustard by Hydrolysis" by C. Reichert, Suffield Technical Note No. 329.

6. "Evaluation of the Suitability of Waste Disposal Sites - Defence Research Establishment Suffield" by D.V. Currie and C. Waterman, Research Council of Alberta. (Contract to DRES).

7. "Disposal of M34 GB Clusters and Mustard Gas at Rocky Mountain Arsenal, Colorado", by LTC Sampson H. Bass, Jr., Director, Weapons Development Engineering Laboratories. EASP 100-78. Proc. of First Meeting on Environmental Pollution 15-16 April, 1970.

8. Visit Report - Visit to CDE Nancekuke, Redruth, England, by S.B. Mellsen - DRES 391-5 (ERS), 5 July 72.

9. Suffield Memorandum No. 59/70, by A.H. Gray & R.V. Jardine. (Title & memorandum classified).

10. "Disposal Methods for Mustard Stocks at DRES", by R.S. Weaver, et al, Jan 73, Suffield Technical No. 328. (Confidential - Not yet published).

11. "Examination of Bulk HS and HT Stocks", by B.G. Cameron, DRES 9930-15-53540 (Chem) dated 9 Aug. 72.

12. "Study of Mustard Destruction by Reaction with Aqueous Sodium Sulfide" by C. Reichert. (Not yet published). Suffield Technical Note STN 242.

13. Reports in preparation on large scale mustard hydrolysis field experiments.

14. "DRES Experimental Proving Ground - Description and Technical Data", Suffield Special Publication SSP 64 (June 73).

15. "Predicting Combustion Products for Disposal of Organic Compounds", by G.A. Hill, Suffield Memorandum No. 41/72.