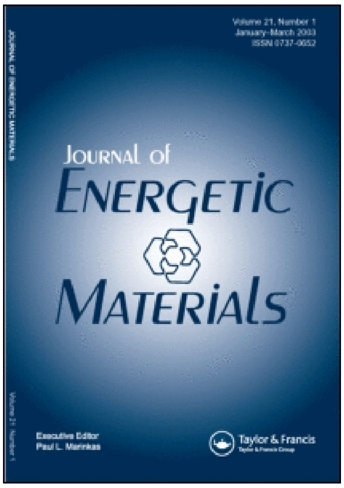

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Disposal of chemical munitions using concomitant neutralization, gelation and encapsulation

Dilhan M. Kalyon[a]; Suphan Kovenklioglu[a]
[a] Highly Filled Materials Institute, Stevens Institute of Technology, New Jersey

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DISPOSAL OF CHEMICAL MUNITIONS USING CONCOMITANT NEUTRALIZATION, GELATION AND ENCAPSULATION

Dilhan M. Kalyon and Suphan Kovenklioglu
Highly Filled Materials Institute
Stevens Institute of Technology
Castle Point on the Hudson
Hoboken, New Jersey 07030

ABSTRACT

The disposal method developed at SIT involves the conversion of chemical munitions to safely transportable inert products. The main advantage is that the need for incineration at every location where currently munitions are stored is eliminated because the neutralized and encapsulated products are capable of safe transport. The method includes the continuous neutralization and gelation of the highly toxic chemicals and the continuous encapsulation of the neutralized products. A preferred embodiment of our disposal method includes a neutralization process which is accomplished by mixing the highly toxic

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chemicals along with any wash solution used to clean out the chemical storage containers or weapons with a neutralization agent specifically chosen to neutralize the particular chemical. The mixing occurs in both a mixing head and in a twin screw extruder designed to ensure thorough mixing.

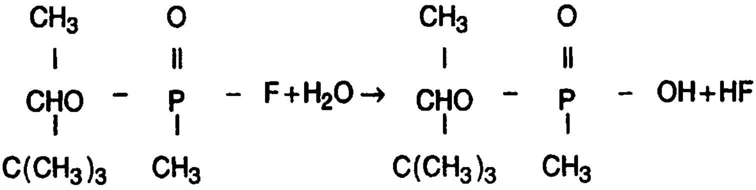
After neutralization, the neutralization products are encapsulated in a polymeric binder via a twin screw extrusion process which is designed to separate the neutralization product into discrete, small sized particles (or droplets), and surround them with the polymer so that the chemical is not exposed to the surface of the encapsulated composition. The encapsulated composition is then coated again with another layer of polymeric material to generate inert "logs" to ensure total encapsulation, and safe transport.

INTRODUCTION

The U.S. Army has a mandate for the disposal of chemical weapons available at its arsenal. Such weapons are present at eight sites in the continental United States and Johnston Island. The Congress has directed the Army to develop and implement a program to safely dispose of the entire chemical weapon stockpile. Current plans of the U.S. Army involve the building of incinerators at each of the eight sites by the year 2000 to dispose of 25,000 tons of chemical agents at an estimated cost of over $8 billion[1].

There is considerable concern to operating incinerators near the population centers[2]. Various alternative disposal options including neutralization/hydrolysis, steam gasification, molten metal/molten salts, supercritical water oxidation, biological methods, base-catalyzed decompositions[3] and concomitant neutralization and encapsulation are proposed as alternatives. In this paper the concomitant neutralization/encapsulation route for safe transport is discussed.

Chemical neutralization has long been recognized as a technique which is capable of significant reduction in toxicity of chemical warfare agents by virtue of the conversion of the parent molecule to harmless products[5-7]. The Army has had extensive experience with alkaline hydrolysis of the agent GB (Sarin)[8]. Other studies suggest that the hydrolysis rates could be significantly enhanced by using catalysts[9-11]. The neutralization of the GB agent is attributed to the hydrolysis reaction where one mole of GB liberates one mole of hydrofluoric acid and one mole of isopropylmethylphosphonic acid:



$$\underset{\underset{\textstyle C(CH_3)_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{CHO}} - \underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle O}{\|}}{P}} - F + H_2O \rightarrow \underset{\underset{\textstyle C(CH_3)_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{CHO}} - \underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle O}{\|}}{P}} - OH + HF$$

When neutralizing GB, in order to prevent the pH level from decreasing due to the formation of acid, NaOH is added. It has been found that the reaction rates correlate with higher pH values. The Army's experience has been that the excess caustic added to speed up the neutralization reaction results in the formation of large amounts of salt (up to 6 pounds per pound of GB).

For the neutralization of the mustard agent the Army finds[8]. monomethanolamine to be more effective. The use of calcium hypochlorite slurry or sodium hypochlorite have also been mentioned to neutralize the mustard agent by oxidation rather than hydrolysis. On the other hand, chlorination in an aqueous acidic medium followed by caustic neutralization has been used for the agent VX. Although the neutralization of the agent GB is attributed to the removal of the fluorine atom from the parent molecule, the neutralization of VX apparently proceeds according to the cleavage of the parent molecule in the hydrolysis reaction[12].

The inherent limitation of chemical neutralization is that complete conversion cannot be achieved in a finite time period. This is due to the significant lowering of reaction rates as conversion becomes very high as well as the difficulty in maintaining a uniform solution concentration of the reactant at such high conversion levels. This is exacerbated by the difficulty in mixing of the partially gelled agent containing solid particles such as rust. For example, the reported half-life value for the agent GB is 0.4 hr. If the first order mass action law were applicable, this would indicate that more than 99.99999% of GB can be converted in a 10 hr batch reaction time, which for all practical purposes can be considered to be complete conversion. However, the Army reports trace levels of GB following alkaline hydrolysis using sodium hydroxide implying that the first order kinetics cannot be reliably used when the reactant concentration becomes very low.

Thus, although chemical neutralization methods for significant reduction in toxicity of GB, VX and mustard agents exist, the inherent inability to drive the reaction to complete conversion (in addition to the necessity to use excess caustic which results in high salt formation) suggests that a hybrid approach for their disposal may be most suitable. The approach proposed here is based on continuous processing involving twin screw extrusion where concomitant gelation, chemical neutralization and encapsulation of the neutralization reaction products into a polymeric matrix take place. Our estimates indicate that a safely transportable product can be obtained.

CONCOMITANT CHEMICAL NEUTRALIZATION AND ENCAPSULATION

The overall method is illustrated in the flowchart of Figure 1. The method involves the application of chemical neutralization, gelation and encapsulation technologies to produce a readily transportable product. Storage vessels or weapons containing munitions are drained of the chemicals and mixed with a purge solution which has been specifically selected to chemically neutralize the particular munitions being drained. Also neutralized at this time is a wash solution which is used to wash the storage vessels or weapons to rid them of the chemical. Next, the purge solution, chemical and wash solutions are further chemically neutralized, converted into a gel and concomitantly encapsulated via two encapsulating polymers. The neutralized and encapsulation solution is covered by a sleeve formation of polymer which is formed around the solution and designed to ensure complete coverage by the encapsulating polymers. The fully encapsulated, neutralized chemical is then encased in sealed containers. It is now ready for safe shipping to a centralized disposal location.

Figure 2 illustrates a diagrammatic representation of a preferred embodiment of the apparatus involved in our method. In a first stage of the apparatus, the highly toxic chemical munitions liquids are mixed in a sealed mixing head with a chemical neutralizing solution of an alkaline aqueous solution selected for its neutralizing properties on the particular toxic chemical. The mixing head allows for the impingement of the munition liquid and the aqueous

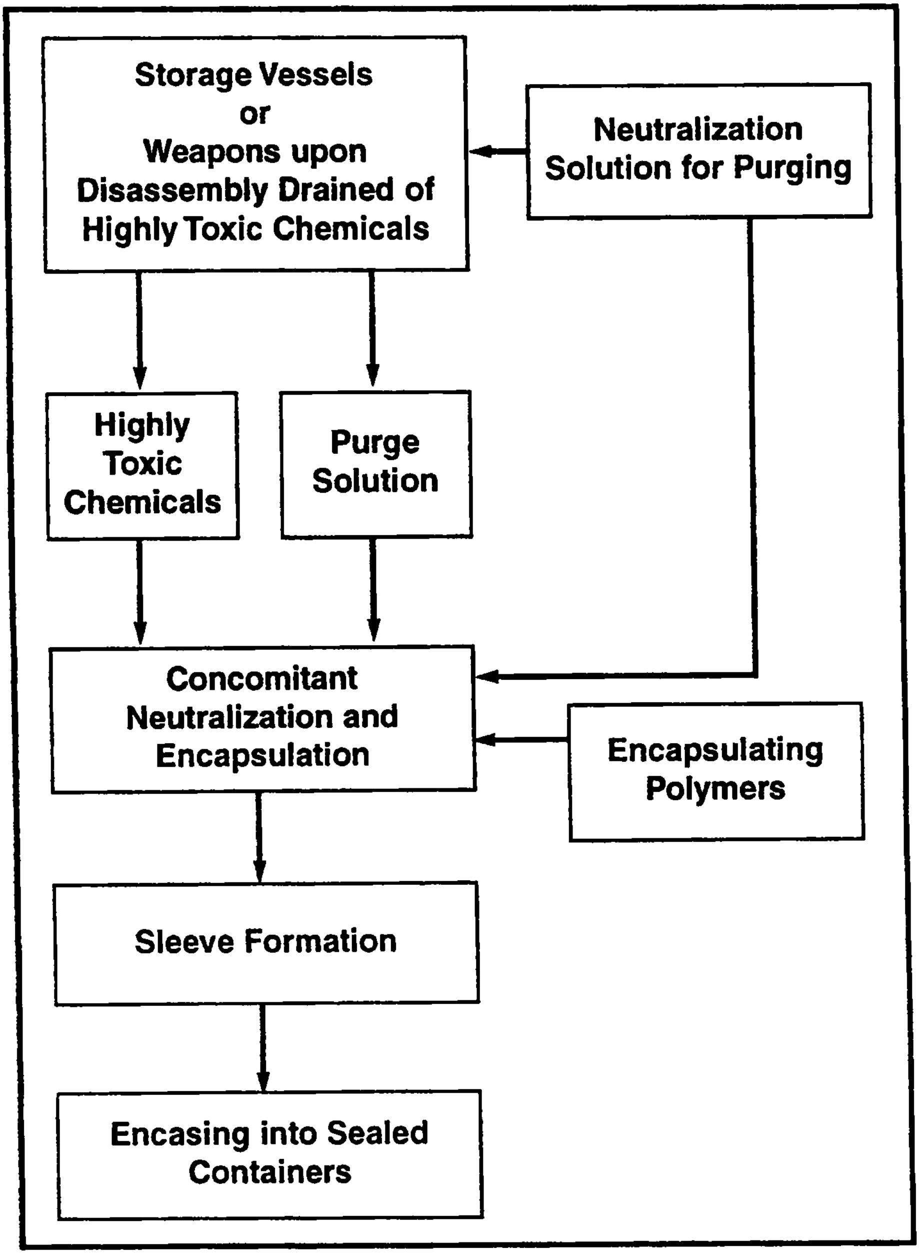

Storage Vessels or Weapons upon Disassembly Drained of Highly Toxic Chemicals
Neutralization Solution for Purging
Highly Toxic Chemicals
Purge Solution
Concomitant Neutralization and Encapsulation
Encapsulating Polymers
Sleeve Formation
Encasing into Sealed Containers

Figure 1

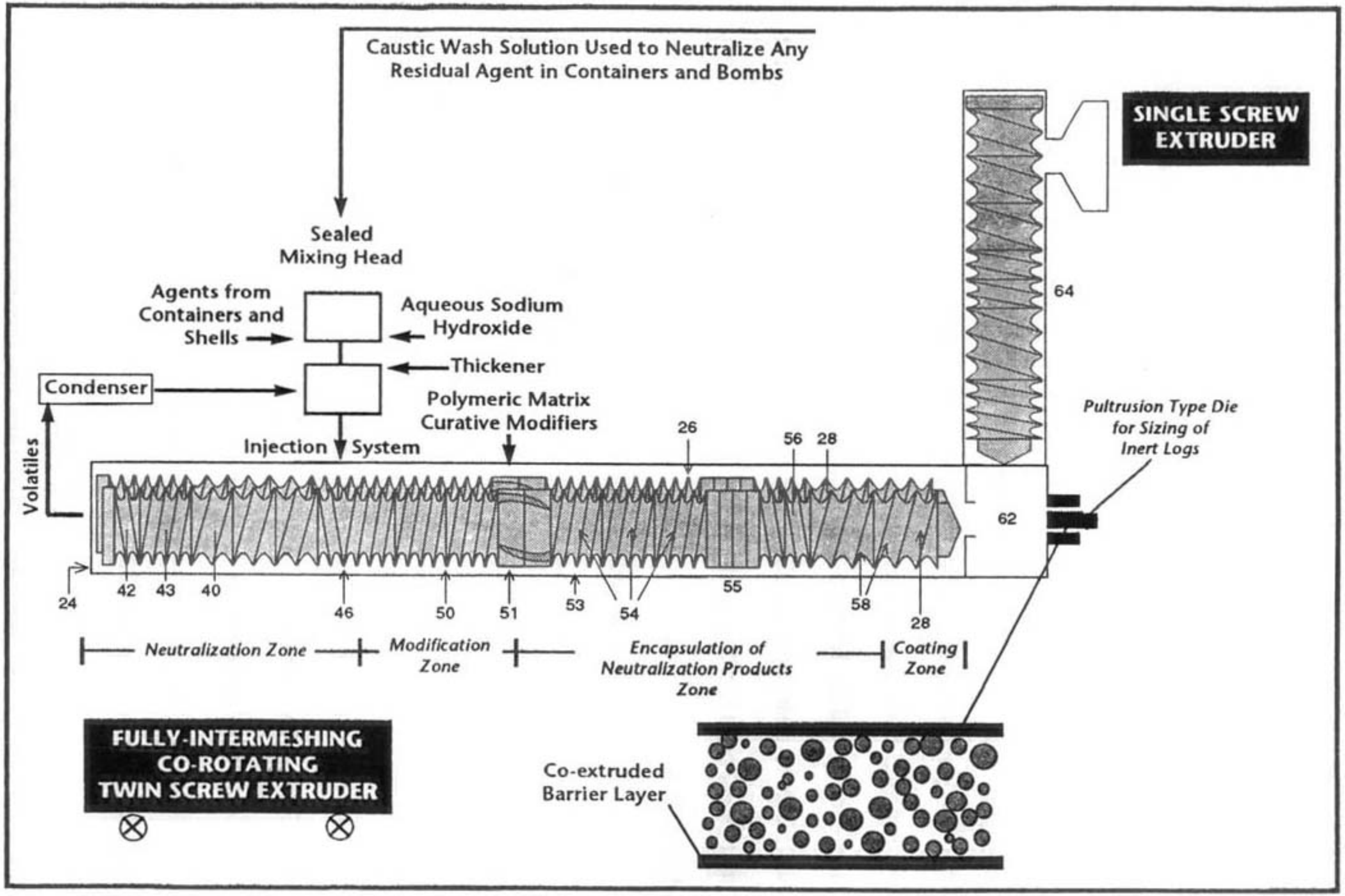

Caustic Wash Solution Used to Neutralize Any Residual Agent in Containers and Bombs
Sealed Mixing Head
Agents from Containers and Shells
Aqueous Sodium Hydroxide
Thickener
Condenser
Polymeric Matrix Curative Modifiers
Injection System
Volatiles
SINGLE SCREW EXTRUDER
64
Pultrusion Type Die for Sizing of Inert Logs
62
26
56
28
24
42
43
40
46
50
51
53
54
55
58
28
Neutralization Zone
Modification Zone
Encapsulation of Neutralization Products Zone
Coating Zone
FULLY-INTERMESHING CO-ROTATING TWIN SCREW EXTRUDER
Co-extruded Barrier Layer

Figure 2

solution, both comprising of liquid streams. To provide sufficient mixing, the impingement velocity values of the streams should be in the regime where the Reynolds number is equal to or greater than 200-500.

A second mixing head is used to incorporate a polymeric thickener into the partially neutralized solution. The thickener is generally soluble in water and increases the viscosity of the aqueous phase so that it will be suitable for processing and also reduce the safety risk. One example of a thickening agent is carboxy polymethylene, which is hydrophilic and water swellable. Our experiments have demonstrated that a water solution of 3% NaOH and 0.5% thickener by weight, for example Carbopol 934 available from BF Goodrich, is sufficient to result in a suitably viscous gel. The gelled mixture of chemical munitions, neutralization agents and thickener is then injected into a co-rotating type twin screw extruder.

In co-rotating twin screw extrusion, the screws rotate in the same direction and are self-wiping. The screws are enclosed in a tightly fitting cylindrical barrel. Thus, a small clearance exists between the barrel and rotating screw elements which prevents the buildup of the materials at the wall of the extruder. A heat transfer medium is circulated within the barrel and/or screw to maintain a constant temperature in the twin screw extruder.

The screw elements of the twin screw extruder are modular and are chosen to accomplish the specific tasks required with respect to a particular chemical munition. Various screw elements are illustrated in Figure 3 and include regular flighted screw sections and lenticular kneading disc "paddles". Also available are neutral disks and devolatilization elements. The elements are each utilized to accomplish specific processing functions, and are configured in an order

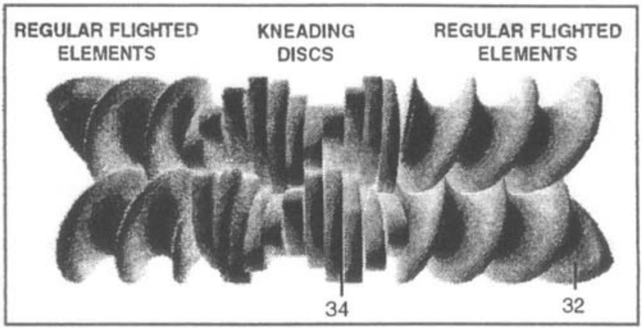


Figure 3

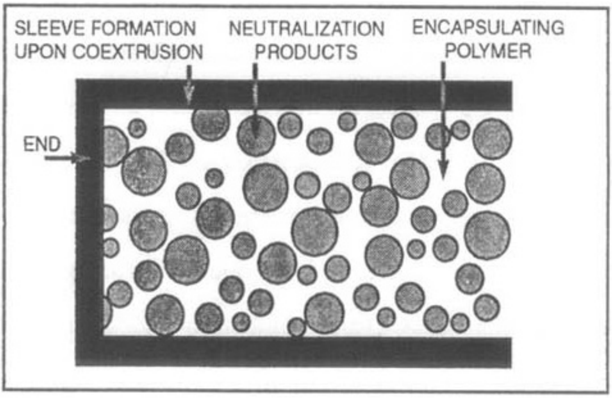


Figure 4

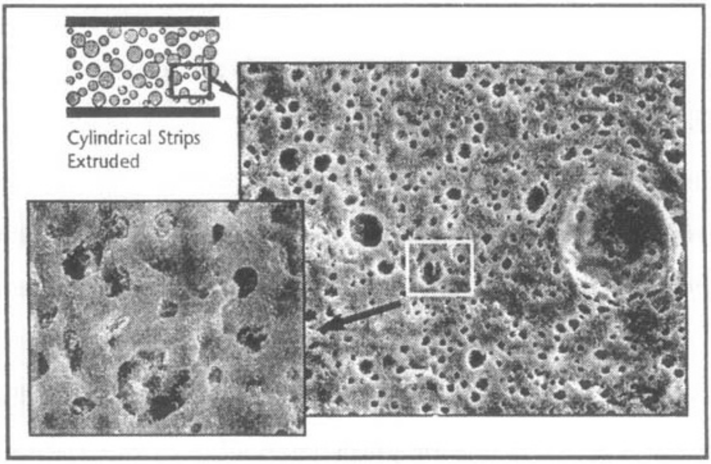


Figure 5

particular to the required processes needed to neutralize and encapsulate a particular chemical.

The screw elements are oriented in both forward and reverse stagger (see Figure 2). When the stagger is in the reverse direction a pressure drop is created in the reverse section which requires a sufficient pressure rise in the mixture in elements preceding the reverse section. Thus, the stagger of the elements creates a means of controlling the pressurization and sealing of the mixture at various locations in the extruder. In addition to the element orientation, screw geometry is variable with respect to screw pitch size, angle and flight size.

Also important in the chemical neutralization and encapsulation are the operating conditions of the system. The operating conditions are monitored via various sensors including temperature thermocouples, pressure transducers, and torque and rotational speed sensors located at various points along the twin screw extrude. The extruder can include characterization equipment such as analytical characterization apparatus which can detail the munitions to be neutralized and encapsulated, and provide suggestions in the selection of screw elements, screw geometry, and operating conditions.

Figure 2 depicts an embodiment of a suitable screw geometry for accomplishing chemical neutralization and encapsulation which generally comprises three zones: 1) the neutralization zone 2) the modification zone and 3) the encapsulation zone. The neutralization zone provides a sealed region where the channel is completely full at both ends, in which the hydrolysis reaction achieves sufficiently high conversions of the chemical munitions to ensure a high degree of chemical neutralization. The mean residence time in the neutralization zone necessary to achieve a sufficiently high conversion of the chemical munition liquid depends on the pH and temperature of the reaction. For example, based on the published first order rate constant for the hydrolysis reaction of GB with caustic at 25°C having a pH of 10 without any catalyst, the estimated residence time for 90% conversion is 40 minutes.[13] The weight ratios of GB to caustic (1N solution) used was 1 to 10. This is higher than the stoichiometric ratio of 1 to 7 and assures an alkaline environment throughout the reaction. It is possible to decrease this residence time by a factor of one half for each 10°C increase in temperature. Thus, a residence time of only 5 minutes is necessary at 55°C to achieve 90% conversion. Various catalysts can be incorporated to increase the neutralization rate even further thus decreasing the residence times.

The residence time of the chemical in the neutralization zone is controlled by varying the screw geometry. For example, in Figure 2, the reverse staggered screw elements are included at the beginning and end of the neutralization zone to provide a pressure decrease which results in a longer residence time. Further, these fully-flighted reverse screw sections are provided to form melt seals around the zone so as to enclose the chemical within the zone and ensure a greater degree of neutralization. However, the neutralization process continues throughout the length of the extruder during the modification and encapsulation zones also.

The neutralization zone begins with a fully flighted reverse staggered screw element to provide sealing of the extruder from the outside (Figure 2). Sealing is provided by the reverse drag created in the flow by the reverse stagger element 42. This element comprises a helix angle of -5.9° with respect to the vertical axis. The diameter of the screw root is 27 mm and the pitch (i.e., axial distance between flights) of the flighted section is 12.7 mm. The element comprises two screw turns.

The reverse stagger element 42 is followed by a forward flighted element 43 having a helix angle of 5.9° with respect to the vertical axis. The diameter of the screw root is 27 mm, the pitch is 12.7 mm, and the channel depth is 11.9 mm. The element comprises 4 screw turns. Following element 43, three double channel forward stagger elements 40 provide mixing and pressurization. The pitch of each element is 25.4 mm and the channel depth is 11.5 mm. The screw root diameter is 27.9 mm, the helix angle is 22.4° from the vertical, and the flight width is 1.5 mm at the tip of the screw. Each element comprises one screw turn. Following the three forward stagger elements 40, another reverse stagger element 46 is included to create a similar seal to the reverse element 42 prior to the modification zone. The specifications of the reverse stagger element are identical to those of element 42. Thus, the mixture is maintained in the neutralization zone via the screw element geometry for the time necessary to neutralize the highly toxic chemical.

In the modification zone, a polymeric matrix, e.g., thermoset for relatively low temperatures, and various modifiers including curing agents and catalysts, are injected into the extruder and mixed with the neutralization products emerging from the neutralization zone. The screw configuration and orientation of the modification zone includes only three forward stagger elements 50 for conveying and premixing the neutralization products with the polymeric matrix. The forward elements 50 have a helix angle of 5.9° with respect to the vertical axis. Each element comprises 2 turns. These elements 50 are followed by a set of ball wing type screw elements 51, at which the encapsulating polymer and other additives are fed into the extruder through a second feed port. The ball wings are included to scrape the surface of the extruder barrel to eliminate stagnant regions.

The encapsulation zone, encapsulates the neutralization products in the polymeric matrix by controlling the configuration and operating conditions of the extruder. The encapsulation zone continues to mix and pressurize the detoxified mixture and the polymeric matrix until the detoxified mixture is reduced to small droplets which are embedded in the polymeric matrix. The orientation and configuration of elements in this zone include the following specifications. One forward stagger element 53 having the same configuration as elements 50 and two forward stagger elements 54 having the same configuration and orientation of the element 43 in the neutralization zone are positioned at the beginning of the encapsulation zone. They continue the mixing process of the detoxified mixture and the polymer matrix and pressurize the melt. The forward stagger elements are followed by a two inch long kneading disk block 55 configured to be staggered at a 60° reverse angle. The kneading discs are used to create better dispersive mixing and to improve the distributive mixing capability. This is followed by two reverse stagger elements 56 which require pressurization at the preceding screw sections to ensure proper mixing of the detoxified mixture and the polymer matrix and provide a melt seal to the encapsulation zone. The reverse stagger elements are followed by two forward stagger elements 58 with a total length of 6". These elements both pressurize the mixture and accomplish the final mixing which encapsulates the small particles of the detoxified mixture in the polymer matrix. Further they allow sufficient pressurization of the encapsulated solution to be shaped into a strand at the die 62.

The die is interfaced to a second extruder. This extruder provides a pressurized polymeric melt to coat the outer surface of the encapsulated mixture as it emerges from the twin-screw extruder i.e., coextrusion. The end of encapsulated "logs" can also be capped with this arrangement. This involves halting the feeding of the chemical and neutralization agents from the twin screw extruder to allow for polymer from the single screw extruder to fill the end sections of the strand thus forming seals as shown in Figure 4. Upon the completion of a run, the extruder is purged entirely by running only the polymeric matrix for a sufficient duration of time to eliminate traces of the previous mixture. Any volatiles which are generated by the process are recycled back to mixing heads, after being cooled in condenser, thus, providing an additional safety feature.

The above-described disposal technology has some inherent safety advantages. Only a small quantity of highly toxic chemical is found in the twin screw extruder at any given time. Other advantages include excellent heat transfer from the high surface to volume ratio in the extruder. The self-wiping action of the twin screw extruder elements provide self-cleaning to avoid formation of stagnant regions. The twin screw extrusion machine is equipped with computerized process control and remote operation and it does not require any manual handling. The barrel of the twin screw extruder has a splitable "clam shell" design with hydraulic actuators to allow for quick release and instantaneous flooding of the contents of the extruder with aqueous alkaline solution.

The process area is continuously monitored for possible contamination with sensors such as broad based solid state sensors. In the event of detection of any chemical warfare agent, the process automatically shuts down. The extent of neutralization can be monitored by determining the total quantity of halogen ions formed during the hydrolization process of GB. Alternatively, in the neutralization of VX, the extent of reaction can be monitored by determining the pH of the sample (pH decreases as hydrolysis proceeds) and comparing it to the estimated pH of the feed. A more accurate approach for monitoring the progress of the reaction is to analyze the parent molecule, i.e., GB, HD or VX through the liquid chromatography/mass spectrometry (LC/MS) technique.

EXAMPLE

The following example describes the results of a series of neutralization and encapsulation experiments performed on the twin-screw extruder apparatus described in detail above. The experiments concerned neutralizing a simulant with NaOH, and encapsulating the simulant with a twin screw extruder in a thermosetting polymer.

Specifically, the simulant comprised of an aqueous solution of 200 ppm (w/w) trichloroethylene. Neutralization was performed by mixing 2 ml batches of 10N NaOH solution with 700 ml of simulant in a well stirred vessel at 100°C for two hours. This resulted in 95% neutralization. The neutralization products were mixed with 0.5% by weight crosslinked acrylic acid polymer to form a hydrogel. To achieve encapsulation, the hydrogel was fed into the twin screw extruder at a constant mass flow rate of 5.6 lb per hour. An epoxy polymer of a diglycidyl ether of bisphenol-A was used as the encapsulating polymer and was fed into the extruder at 8.4 lb per hour. A curing agent of precatalyzed trifunctional mercaptan based hardener with tertiary amine was also fed into the extruder at 8.4 lb per hour. The extruder was maintained at 57°F with a screw speed of 30 rpm.

Upon completion of the screw operations the formulation was well mixed, as is evident from Figure 5 which is a micrograph of the extruder products of the above-described example taken by a scanning electron microscope and magnified 2,000 times. The hydrogel which contained the neutralization product was thoroughly and uniformly mixed with the epoxy polymer and finely dispersed in the polymer. Specifically, the mean diameter of the hydrogel deposits were approximately 2.4 micrometers and the mean distance of epoxy polymer between hydrogel deposits was approximately 4.4 micrometers. Thus, hydrogel drops were well encapsulated in the epoxy polymer. With the use of a second extruder to cover the formulation with a 5-15 mm coating of encapsulating polymer (the conventional and well-known co-extrusion process described above), the formulation would be sufficiently encapsulated so that it would be safe for transport. The permeation versus thickness of the encapsulation thickness issues are discussed next.

PERMEATION THROUGH THE POLYMERIC BARRIER

In order for the encapsulated material obtained with the proposed technology to be safe for transportation, the time required for any residual chemical warfare agent to diffuse through the polymeric barrier should be sufficiently long. To estimate the time it takes for the solute molecule to travel through the polymeric barrier, the diffusion coefficient of the solute in the polymer needs to be known. This information is not available for chemical agents. However, diffusion coefficients of a wide range of solutes in different polymers have been found to range from 10^{-6} to 10^{-9} cm^2/s (14). The higher diffusivity range would correspond to smaller molecules and those which tend to solvate the polymer. Diffusion through polymeric solids is envisioned to occur by "jumps" from one position to another over a potential barrier with the successful jump requiring that a hole of sufficient size is available (14). Hence, the larger molecules of chemical agents are expected to have lower diffusivities. In addition the chemical agents which are typically organic esters of substituted phosphoric acid are not expected to have the solvation tendency of conventional solvents. Consequently, we can consider a solute diffusivity value of 10^{-8} cm^2/s to be a conservative estimate. Corresponding to this diffusivity, the diffusion time, t, across a polymeric layer of 15 mm can be calculated from $t = L^2/D$ as over seven years.

It is noteworthy to observe that diffusion time increases with the square of the diffusion distance and that pockets of encapsulated solution away from the edges would have longer diffusion times than those near the edges. The encapsulation technique has the flexibility to increase the diffusion distance for regions of encapsulated solution near the edges (by coating additional outside layers) as well as the distance in between the pockets of encapsulated solution (by adjusting composition). It should also be pointed out that the neutralization reaction is expected to continue within pockets of encapsulated solution, although at a slower rate due to the absence of mixing. This observation, along with the possibility that actual diffusion times may be much longer than the conservative estimate here, may well make the option of indefinite storage at site environmentally acceptable. It should, however, at the minimum, make safe transportation for ultimate disposal viable.

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