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Dusty Agents and the Iraqi Chemical Weapons Arsenal

Introduction

The New York Times recently reported that an Iraqi defector—known under the pseudonym of Ahmed al-Shemri—has provided the West additional intelligence on development activities in Iraq regarding nerve agents, including VX.[1] According to al-Shemri, since 1994, Iraq has devised and produced a solid VX formulation that could be described as a "dusty" agent. The properties of this agent include the ability to adhere and penetrate gaps in chemical-protective garments. Having a high persistency and the capacity to poison through the skin, such a preparation of VX could pose an extreme danger to U.S. troops, as well as complicating decontamination efforts.

This issue brief provides the relevant historical and technical background to properly assess the significance of this disturbing report. It first summarizes the history of Iraq's chemical agent production—including VX—and then details the key technical and military issues related to the deployment and use of chemical agents more generally. The brief concludes by describing the exceptional toxicity of VX agents and the enhanced military utility of VX and other chemical weapons when they are "thickened" to make dusty agents.

Background of Iraqi CW Agent Production

During the Iran-Iraq War (1980-1988), Iraq developed, deployed, and used significant amounts of chemical weapons (CW) against Iranian forces, as well as civilian targets in Kurdish-held territories. Beginning in about 1984,[2] Iraq made extensive use of mustard (blister) and tabun (nerve agent), probably having chosen these compounds because they were the easiest to produce.[3] Throughout the conflict, Iraq used an estimated 3,000 tons of CW agents of various kinds, employing more than 100 tons in certain individual military operations.[4] Based on UN Special Commission (UNSCOM) inspections of Iraqi weapons following the Gulf War of 1991, Iraq also produced tons of VX and weaponized this CW agent into a variety of delivery platforms, including artillery rockets (e.g., 122 mm) and Scud warheads (see sidebar).

There is also considerable evidence that Iraq employed a "dusty" form of mustard in the war with Iran. This dusty formulation utilizes a solid carrier—such as silicon dioxide or talc—that can create breathable aerosols of mustard agent. It is not surprising that Iraq might direct its efforts towards new formulations for delivering CW agents, possibly including nerve (VX) agents.

Iraq's Strategy of Denial

Lying about its past and present chemical and biological weapons programs has been the constant strategy for Iraq over the past 20 years. For example, on April 1, 1985, after UN investigators concluded with solid physical evidence that Iraq had used chemical warfare against Iran, then-Foreign Minister Tariq Aziz flatly denied it at a press conference in Tokyo.[5] Similarly, when the United States and the United Nations had determined that Iraq had weaponized Scud warheads with VX nerve agent in 1998, the Iraqi Foreign Minister Mohammed Saeed al-Sahhaf called such an allegation an "imaginary monster they created in their sick minds." [6]

Although reportedly contradicted by tests carried out in France and Switzerland, the results of the U.S. laboratory tests on Iraqi VX scud warhead fragments offers incontrovertible evidence of not only VX, but also a substance used to keep the nerve agent stable—in other words, the nerve agent had been weaponized. (For more details, see "Iraq Special Collection: UNSCOM's Report on Iraqi VX Warheads," October 1998.)

Iraq had already declared in 1996 that it had produced VX at the Dhia plant in the Muthanna State Establishment, and that nearly four tons of VX had been manufactured. Iraq reported that all of this had been dumped in the "grave yard" at the Muthanna State Establishment. However, Iraq had consistently denied that it had ever weaponized VX.[7] Before they were discovered by UNSCOM inspectors, the VX from Scud metal remnants had been destroyed or decontaminated by the Iraqis in an attempt to get rid of the evidence; however, from the analysis of trace degradation products and other chemical compounds found on missile warhead fragments, the United Nations was able to determine that Iraq had loaded VX on "special warheads" with dicyclohexyl carbodiimide (see below), a compound that has long been known as a VX stabilizing compound.[8]

Below are some details of the fragments that were tested, the chemicals that were found, and explanations of their significance. Of the fragments, RQX002 is representative. Among other breakdown products, this metal shard contained dicyclohexyl carbodiimide (CAS 538-75-0); its chemical structure is shown here: The other chemical compounds that were detected by the U.S. Army Laboratory in Aberdeen Proving Grounds, Maryland included O-ethyl methyl phosphonic ester (EMPA) and N'-diisopropyl aminoethyl sulphide (shown in the UNSCOM document at RSR). These two degradation products originally formed the original VX molecule, with EMPA shown here in red, and the other portion in blue:

VX molecule showing the O-ethyl methyl phosphonic ester portion (red) and the N'-diisopropyl aminoethyl sulphide (blue).

Because the sulfur portion of the molecule serves as the so-called "leaving group," it follows that VX would have degraded into these different compounds.

Difficulties in Weaponizing and Delivering CW

Both during and since World War I, many militaries have actively sought toxic compounds that could create more casualties on the battlefield. While poisons such as cyanide, arsenic, nicotine, and carbon monoxide have long been recognized, these were not effective as weapons in modern warfare. Indeed, due to various physical, chemical, and toxicological properties, most chemicals were limited in their ability to cause death or injury on the battlefield. They were either too volatile, as was the case of hydrogen cyanide, or were simply not toxic enough to do much damage.

Obviously, the technical difficulties encountered when delivering CW agents come as a result of the physical state of a given chemical compound. Depending upon whether a CW agent is solid, liquid, or gaseous at room temperature can determine the method of its delivery. For example, the first major success in a chemical attack involved the use of chlorine gas at Ypres, Belgium, in 1915 during World War I. In this true "gas" attack, chlorine (Cl_2) was brought to the front lines in liquid form, stored under pressure in metal cylinders. When the valves of the cylinders were released, the chlorine was allowed to rapidly evaporate into a gas. From the perspective of CW delivery, this approach had some drawbacks, however. In addition to the great effort required in transporting large quantities of chlorine-filled cylinders to the front, German military personnel carrying out this attack had to wait for suitable weather conditions, relying upon the wind to carry the gas to the enemy. Because chlorine is a gas at room temperature, it is naturally quite volatile. Chlorine also dissipates rapidly with air currents, and is not as toxic as many other CW agents that were devised later. But being heavier than air, chlorine drifted along the contours of the battlefield, filling trenches and revetments. In this first major chemical assault of World War I, chlorine gas probably killed about 800 Allied soldiers.

Other attempts during World War I and afterwards to use toxic chemicals have involved hydrogen cyanide (HCN), or prussic acid. This compound is nominally liquid at room temperature, but rapidly evaporates into the air. (Having the property of readily forming vapors made it an effective rodenticide for barns and other structures. It was from this usage that Zyklon B, the instrument of the Holocaust, was devised.) In fact, HCN evaporates so quickly that it carries away large amounts of heat while doing so. A drop of HCN on a flat surface at room temperature will convert to a small, congealed spot that freezes due to the cooling effect of its vaporization. In order to devise a weapon to deliver HCN, one must overcome the extremely volatile nature of this chemical in order to increase the concentrations of the poison gas. During World War I, the major belligerents tried to use HCN, without much in the way of practical results. During World War II, some Japanese soldiers were equipped with glass jars filled with liquid HCN that had been stabilized with copper or arsenic trichloride. (Frangible as these grenades were, just carrying them must have been an extreme hazard.) Again, we are not aware of any Allied deaths caused by these chemical "bombs." Thus, the problem of using CW agents has also largely been one of their persistence—or rather a lack of it. The trick has long been to deliver large enough concentrations of a CW agent in a given area, and for this concentration to remain potent over a long enough period of time to achieve the desired results. The initial successes in World War I with gases such as chlorine and phosgene quickly led both sides of the conflict to adopt protective measures. Literal "gas" warfare could then be defended against with improvised masks. (In the early days of CW during World War I, this often involved urinating on rags and holding these over the

mouth.[9]) Once the Western militaries figured out that CW agents were being used in attacks, the implementation of simple protective measures (masks) made chlorine by itself largely ineffective throughout the rest of the war. Furthermore, being gaseous at room temperature, these toxic compounds quickly dissipated into the atmosphere. Until mustard was introduced in 1917, the myriad CW agents used at the time were largely incapable of causing much injury except through inhalation.

Liquids that do not easily form vapors can be delivered more effectively in the form of an aerosol—that is, a suspension of fine particles in the air—which can create larger concentrations over a target. One can generate aerosols by forcing liquids through a specially designed nozzle. Detonating an explosive shell containing a CW agent also creates a combination of aerosol and droplet-sized particles. Depending on the average diameter size of the particles, aerosols can drift and cover large areas, and in this sense, behave much like gases. Very tiny particles will remain aloft for considerable periods of time, depending upon the relative stability of airflows. While all objects eventually fall to the ground, very light particles—those weighing 1-2 microns—will fall less than one centimeter per minute due to air resistance.[10] For weapons designers, however, aerosols also pose some other challenges, namely that of wind drift.

Some CW agents developed during and since World War I have been solids at room temperature. In the latter stages of the war, the German military put great efforts into the production of diphenylcyanoarsine (DC), a so-called "arsenical" that was irritating in very small concentrations. One of the strategies involved in using this substance was to render gas masks ineffective. This was to be achieved by delivering DC in a fine aerosol, producing very small particles that would penetrate the filters used in protective masks at the time. [11] The goal would be the forced removal of the mask, thereby making the enemy vulnerable to further assault with other toxic agents. However, it proved difficult to deliver these sternutators, or "sneeze" gases, in particles small enough to achieve this effect, and in this regard, DC was not very successful.[12]

Because enemy defensive masks could not be defeated with arsenical compounds in World War I, the German military command investigated other alternatives. Mustard proved to be the answer. Sulfur mustard had been known since the 1880s as being a very toxic compound to exposed skin surfaces,[13] and as a contemporary historian wrote:

"...there was still another reason that led to the introduction of mustard gas in chemical warfare. This was the length of time mustard gas remains un-decomposed in the field. It is this quality which made it fit for defense. The decisive animal experiments on mustard gas [using cats and dogs] were made in September and October 1916. The valuable military qualities of this gas were already known, when the High Command of the German Army demanded a gas that could be used for the defense of the Western Front in the coming summer of 1917."[14]

Although described here as a gas, sulfur mustard is in fact an oily liquid. Sulfur mustard can cause injury by vapors, inhalation of aerosols, contact with contaminated surfaces—or a combination of all these. Mustard is fat-soluble and able to penetrate clothing (including some forms of rubber), making full-body protection necessary. The toxicological effects of mustard are furthermore insidious, causing blisters on the skin, temporary blindness (sometimes with permanent loss of vision), and life-threatening damage to the upper airways. Such symptoms occur within hours of exposure.

Even today, mustard remains one of the top CW agent threats, not just because of its versatility as a weapon, but because it is relatively cheap and easy to make. It is therefore not surprising that Iraq made extensive use of mustard against both Iranian forces and Kurdish elements during the Iran-Iraq War, from about 1983 to 1988. Although Western countries (led by the United States) cut off exports of mustard precursors to Iraq and Iran in 1984,[15] by adapting its own petroleum distillation capabilities, Iraq was able to indigenously

produce sulfur mustard.[16]

For all of its strengths, however, mustard is not as toxic as the nerve agents developed in Germany during the 1930s, nor is it as fast-acting (hours in the case of mustard versus minutes for nerve agents).

Nerve Agents: G-series Compounds and V-agent Analogues

Discovered in the course of investigating novel organophosphate compounds for use as insecticides, German chemists synthesized tabun in 1937, which was later incorporated into the German chemical munitions stockpile during World War II. Later, sarin, soman, and other derivatives were synthesized. None of these was used, however, and the West only discovered their existence upon the end of the war.

In early 1951 during the Korean War, U.S. Army hygienists first noted strong resistance in lice to DDT when delousing North Korean POWs and refugees.[17] When DDT and other organochlorines lost their effectiveness, chemical firms such as Bayer and Imperial Chemical Industries sensed that the market was especially ripe for new and better replacements, including the use of organophosphorus compounds as insecticides.[18] When Ranajit Ghosh patented novel compounds that later formed the basic structure for VX in the early 1950s, the intent was to develop effective insecticides that were also safe for mammals. Some of his new inventions, however, were quite toxic to mammals as well as insects. The V-series of agents (V="venom") were clearly more geared for pests of the "two-legged variety."

Even for a nerve agent, the extreme toxicity of VX, as well as its physical properties, are quite exceptional. First, its lethality for a 70 kg man (155 lbs) is estimated somewhere between 10 and 15 milligrams, an extraordinarily small amount. Second, it is also quite persistent, and depending upon environmental conditions, will survive in its toxic form for days or weeks. However, being 12 times less volatile than mustard, VX does not readily form vapors. While it excels in its high persistency, it is difficult to do more than contaminate ground or materiel with VX. In order to expose larger numbers of enemy troops to VX, an aerosol would be more effective against unprotected troops than, for example, merely splashing large droplets of the agent on the ground.

Thickening Agents

Militaries have investigated ways to change the physical characteristics of a CW agent to improve its delivery performance. Part of the approach is to adjust certain behavioral traits of a given compound, using polymers and other chemical additives to change surface tension, densities, storage parameters, and shear rates (i.e., droplet formations from rapidly-moving delivery platforms).[19] These new formulations can also make decontamination more problematic for the enemy.

A number of compounds have also been utilized to make some agents thicker and thus more persistent. As in formulations of napalm since World War II, these additives can also be used to increase the capacity of CW agents to cling to people or materiel. In 1969, for example, the U.S. military applied for a patent to thicken a number of CW agents—including tabun, sarin, soman, and VX (nerve) as well as Lewisite, and Lewisite-mustard mixtures (vesicants)—with a polymer/thickener. Such a preparation promised to "provide a new and useful composition of matter particularly adapted to adhere to and prolong the level of contamination in the treated area." [20] Although probably not showing its most sophisticated repertoire, the Soviet Union's exhibition of its chemical weapons at Shikhany in 1987 may have come as somewhat of a surprise to Western observers who did not know that the Soviets had also thickened soman, VX, and even Lewisite with some sort of polymer.[21] There has also been the suggestion that U.S. binary nerve programs—canceled in the 1990s—would have involved thickeners for soman and VX.[22]

Having thus far involved liquids or jelly-like preparations, these above techniques can be used to make CW agents more persistent and less susceptible to decontamination. Dusty agents, on the other hand, involve the use of solid materials to produce aerosols. Not only do dusty agents increase the amount of agent that can be spread across an area, they can also frustrate and defeat chemical-protection measures. While it is possible that Iraq has continued work with dusty VX,[23] it may also have worked with other formulations to increase the persistence of VX.

Dusty Mustard and Dusty VX

The term "dusty mustard" or "dusty VX" refers to the use of a carrier particle such as talc or diatomaceous earth in order to form a particulate aerosol out of these liquid agents. There are commercial applications for similar preparations, such as insecticides used in households and gardens against pests such as ants, fleas, and ticks. Ortho® Ant-Stop, for example, uses an organophosphate (chlorpyrifos) insecticide impregnated on an inert carrier that is safe for use around mammals and people. This dust is prepared in a relatively fine particle size distribution,[24] and can be delivered into tight spaces. The dust finds its way into nooks and crannies that other types of delivery could not reach.

In CW, the use of carriers can be applied to bring about the dissemination of chemical agents in the form of aerosols. In this way, one can ensure a larger area of coverage with an agent. Although individual particles are quite small, and would not carry much in the way of agent dispersed as a large, concentrated cloud, many more particles will cumulatively impact upon enemy soldiers and equipment, contaminating both. For mustard and VX—both fat-soluble agents that can also cause injury through contact with skin—dusty agent formulations increase their ability to poison through the respiratory system, and also exploits weak points in chemical defensive gear. Although protective masks can prevent much of the inhalation hazard, the greatest danger is created by fine particulates making their way into gaps and spaces of clothing—no matter how well these are fitted.[25] Accumulations of fine dusts may defeat even full-body protective garments, and coupled with the dermal action of VX nerve agent, they represent a significant military threat.

In 1990, U.S. intelligence reported that Iraq had used mustard in a "particulate aerosol form" in its war with Iran during the 1980s. It further noted that Iraq could have also produced a dusty nerve agent formulation, but there was "no evidence that it has done so." One of the more menacing aspects of this information, albeit unconfirmed, was that a dusty V-agent could cause "fatalities ranging from 3 to 38 percent...for troops in full MOPP [NBC protective gear] if such an agent were used." [26] The U.S. Army then suggested that the wearing of a poncho over the NBC garment would aid in protecting against dusty agents, although one gets the sense that this was recommended in the face of few other options.[27] With a concern that dusty agents might defeat chemical protective masks and garment ensembles, U.S. military researchers subsequently looked to topical skin protectants for additional protection against dusty agents.[28]

A U.S. military report from 1991 noted the capture of Iraqi weapons stores that included dusty mustard ordnance. During the ground campaign of Desert Storm on February 26, 1991, inside the Kuwait theatre of operations, Task Force Ripper reported having found "dusty mustard found stored in bunker." [29] During the 1990s, however, UNSCOM inspections in Iraq did not turn up much more information on Iraqi work in dusty agents. According to an April 2002 report delivered by Robert D. Walpole, Special Assistant to the Director of Central Intelligence for Persian Gulf War Illnesses:

"UNSCOM information shows no research or production of dusty agents in the years prior to the war, although a handwritten note found by UNSCOM indicated that an Iraqi was considering the idea in the late 1980s. UNSCOM tested a DB-2 bomb in 1997 because of concern it was filled with dusty sarin, but found

only that it had been incompletely decontaminated and that solids had formed from reaction of the bomb's metal casing with an impure sarin mixture." [30]

Conclusion

Because Iraq has proven artillery systems for chemical delivery, the alleged Iraqi development of a dusty VX formulation further increases the chemical exposure risks to U.S. troops that may be operating in theatre. Considering the very high toxicity and persistent nature of VX nerve agent, the hazard presented by dusty VX is significantly higher than VX delivered in the conventional manner. When it comes to force protection during actual fighting on the ground, the threat from dusty VX will only make U.S. military planners redouble their efforts to ensure that their protective suits and masks will sufficiently safeguard U.S. and allied troops.

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