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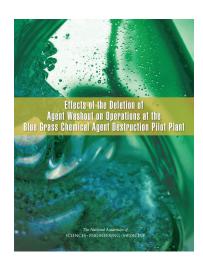
Effects of the Deletion of Chemical Agent Washout on Operations at the Blue Grass Chemical Agent Destruction Pilot Plant

s part of the U.S. effort to destroy its remaining stockpile of chemical munitions, the Department of Defense (DoD) is building the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) on the Blue Grass Army Depot (BGAD) near Richmond, Kentucky. The stockpile stored at BGAD consists of rockets and projectiles containing the nerve agents GB (sarin) and VX and the blister agent mustard. Due to public opposition to the use of incineration to destroy the BGAD stockpile, BGCAPP will destroy the GB and VX by hydrolysis using hot caustic solution, and the resulting hydrolysates will be further treated using supercritical water oxidation. The original BGCAPP design called for the munitions to be drained of agent, and then for the munition bodies to be washed out using high-pressure hot water. However, the munition washout step was later eliminated in response to concerns that the mixture of agent and wash water could potentially compromise safe operations and impede processing throughput. This modification will cause larger quantities of agent to be partitioned into different BGCAPP systems that were designed to treat only small amounts of residual agent, complicating the plant's ability to achieve and demonstrate the required destruction efficiency (DE). At the request of the DoD's Program Executive Office for Assembled Chemical Weapons Alternatives, the National Academies of Sciences, Engineering, and Medicine produced this report to assess the impact of this design change on plant operations, provide suggestions for confirming DE, and recommend where additional modeling may be beneficial.



Decades in storage have caused the agent fills to degrade and its physical state to change, which can affect agent drain times. Because agent degradation varies by agent type and manufacturing lot, better data are needed to properly estimate the time needed to drain the nerve agent from munitions.

RECOMMENDATION 2-1: BGCAPP should gather data, such as mass drained, drain time, and any available information on physical state, for each individual munition during operations ramp up to assess the state of the agent fills and thus expected variability in drain times for each agent lot and type of munition. The acquisition of these data should continue



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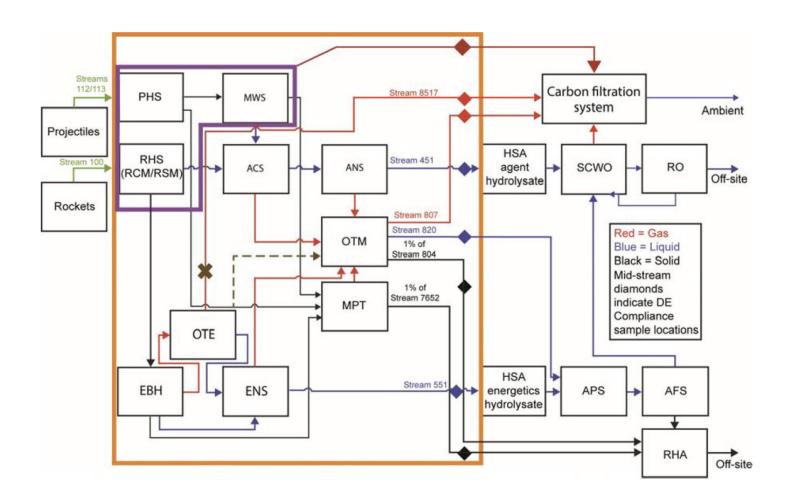
For Projectiles

After the agent is drained, projectile bodies are processed through the metal parts treater (MPT), which thermally decontaminates them. The gaseous effluent from the MPT flows into the plant off-gas treatment system (OTM). With the removal of the washout step, the drained projectile bodies will contain significantly more residual agent than planned, which means that agent processed through the MPT and the OTM will constitute a potentially significant fraction of the agent destroyed at BGCAPP.

RECOMMENDATION 2-2: BGCAPP should evaluate whether higher agent vaporization rates in the MPT can be accommodated by optimizing the operating parameters of the MPT, the off-gas treatment system, and associated systems.

For Rocket Warheads

After rocket warheads are drained and sheared, the pieces are sent to energetics batch hydrolyzers (EBHs) that access and hydrolyze the energetics in the warhead bursters with hot caustic; this will also destroy residual agent. With the deletion of munitions washout, more chemical agent will be sent to the EBHs and to the EBHs off-gas treatment system (OTE) than originally planned. While the OTM is equipped



Flow diagram showing committee recommendations for expanding effluent measurements to allow the calculation of DE at 99.9999 regulatory requirements and for rerouting the OTE through the OTM. The orange and purple boxes represent the committee's interpretation of the measurement of BGCAPP effluents to be used in calculating the DE of 99.9999. The purple box around the MWS, PHS, and RHS, and the unnumbered maroon line from the purple box to the carbon filtration system represent fugitive agent emissions from munition drain operations, which are sent directly to the carbon filter banks. The brown dotted line represents the committee's recommendation that OTE emissions be routed to the OTM; and the brown X on the red line directly out of the top of the OTE box represents the committee's recommendation to delete this stream upon rerouting to the OTM. SOURCE: Adapted from J. McArthur, environmental manager, BPBG, "Destruction Efficiency Considerations," presentation to the committee on September 9, 2015.

with a thermal oxidizer (TOX), which will likely be able to destroy agent vapors, the OTE does not have a TOX so some agent may flow into the building HVAC system and be captured on the carbon filter banks.

RECOMMENDATION 2-3: BGCAPP should conduct modeling and experimental studies to bound the quantity of agent present in the OTE vent stream (stream #8517).

RECOMMENDATION 2-4: BGCAPP should complete modeling to estimate the agent load to the carbon beds in the absence of a munition washout step to ensure the lifetime of these beds is known.

DEMONSTRATING DESTRUCTION EFFICIENCY

BGCAPP is legally required by Kentucky law to achieve what is termed "six-nines" destruction efficiency of GB and VX, which means that it must be demonstrated that the 99.9999% of the agent has been destroyed. With washout deletion, the current methodology for calculating DE will no longer be applicable because an increased fraction of agent will now be sent to secondary systems such as the EBHs. Destruction efficiency of agent in these secondary systems is not explicitly known and will need to be demonstrated in order to provide a defensible calculation of DE.

RECOMMENDATION 3-1: BGCAPP should calculate or otherwise demonstrate a 99.9999 percent ("six-nines") destruction efficiency (DE) for residual agent residing on rocket warhead pieces exiting the MPT. This would provide assurance that the solid effluent from the MPT (stream #7652) generated during rocket campaigns is free of agent to ensure compliance with DE requirements.

RECOMMENDATION 3-2: BGCAPP should demonstrate satisfactory destruction efficiency for agent serially treated with caustic under the same conditions as those present in EBHs and the energetics neutralization system at agent loadings equivalent to the highest quantities anticipated to be treated by the EBHs without washout.

BGCAPP personnel have considered two alternative methodologies to determine DE, but these entail much more measurement, and, in many cases, good analytical methods do not currently exist. With some streams, like the caustic in the EBHs, it may be difficult to measure agent concentration down to a level that would demonstrate achievement of the DE criteria. While counting the agent trapped in the Munitions Demilitarization Building (MDB) heating, ventilation, and air conditions (HVAC) carbon beds as destroyed might be an attractive solution, the Kentucky Department for Environmental Protection has stated that BGCAPP may not take credit for measurements downstream of the car-

bon filtration system without revision to Kentucky statutes/ guidelines. Therefore, under current law, agent trapped in the MDB HVAC carbon beds cannot be counted as destruction in the calculation of DE.

RECOMMENDATION 3-3: For all of the gaseous process streams, BGCAPP should rigorously demonstrate that negligible agent is partitioned into the MDB HVAC carbon filter banks under all conditions that could arise during the rocket campaign. BGCAPP should provide for monitoring of the OTE effluent stream (#8517) with analytical sensitivity sufficient to ensure that destruction efficiency criteria are achieved before they enter the MDB HVAC system.

One potential solution to the uncertainty about the OTE's ability to destroy any residual agent from the EBHs would be to route the OTE effluent through the OTM, to take advantage of the TOX to destroy any residual agent.

RECOMMENDATION 3-4: BGCAPP should examine the possibility of routing the gaseous effluent from the OTE into the OTM. This would eliminate the biggest uncertainties in M_{out} exiting the MDB, because it is likely that any agent surviving the OTE would be destroyed in the OTM. The number of gaseous streams from processing units exiting the MDB would be reduced to a single stream—namely, the off-gas from the OTM—and would be less likely to contain significant agent as a result of off-gas passing through the thermal oxidizer.

It is likely that the combination of the MPT and the OTM will completely destroy any agent entering the MPT. However, after washout deletion, the OTM will receive gaseous streams from other sources that may contain more agent than originally planned. It is currently unknown whether the OTM can adequately treat the combined load of all streams after washout deletion.

RECOMMENDATION 3-5: BGCAPP should measure solid, gaseous, and liquid effluents from the OTM during initial projectile campaigns to ensure that these effluents meet the destruction efficiency criteria.

An alternative approach for demonstrating DE, called Approach 3, would involve measuring agent quantities in the effluent streams from all treatment units. This approach would require development of additional methodologies for measuring masses of agent partitioned into the two gaseous waste streams entering the MDB HVAC system. The performance requirements for measuring agent in the off-gas process stream from the OTE are not known because the fraction of agent that will be partitioned into this stream is uncertain.

RECOMMENDATION 3-6: If Approach 3 is adopted, then BGCAPP should evaluate the concentrations of agent liable to be present in all gaseous process streams and develop measurement approaches with sufficient sensitivity to ensure that destruction efficiency criteria are being achieved.

RECOMMENDATION 3-7: If Recommendation 3-4 is not pursued, BGCAPP should conduct research to determine what fraction of GB agent might partition into the off-gas process stream from the OTE, and then use this information to set analytical performance requirements that can be used to identify analytical measurement methodology.

MODELLING TO PREDICT THE IMPACT OF PROCESS CHANGES ON OPERATIONS

While the current process model of BGCAPP explores how changes in operating parameters affect overall performance, it does not reflect the expected variability in plant operational parameters. Analysis of the sensitivity of BGCAPP operations to variations in model input parameters might expose potential operational issues, allowing them to be quantified and possibly mitigated prior to operations. For example, the time to change out the filter socks used to capture agent solids may be the most important rate-limiting factor in BGCAPP operations and may be underestimated.

RECOMMENDATION 4-1: BGCAPP should retrieve and document historical (informal and anecdotal) data on munition drain times and run these data, complete with ranges of uncertainty, through the BGCAPP model.

RECOMMENDATION 4-2: BGCAPP should design and execute a series of modelling experiments to determine the sensitivity of operations to variations in operating parameters, reflecting the stochastic nature of some processes. Examples of parameters include maintenance and repair times, added characterization steps, retreatment for batches not meeting destruction efficiency, and compounding problems such as long munitions drain times together with very frequent filter sock change-outs. The results of these experiments should be used to prepare for potential challenges and mitigate them ahead of time as much as possible.

RECOMMENDATION 4-3: During start-up, and continuing through plant operations, BGCAPP should gather data for relevant model parameters with sufficient resolution to assess the probability density functions for these parameters.

RECOMMENDATION 4-4: BGCAPP should give attention to developing analysis tools such as statistical quality control prior to actual facility start up.

COMMITTEE ON EFFECTS OF THE DELETION OF CHEMICAL AGENT WASHOUT ON OPERATIONS AT THE BLUE GRASS CHEMICAL AGENT DESTRUCTION PILOT PLANT: Gary Groenewold, Idaho National Laboratory, Chair; Herek Clack, University of Michigan, Ann Arbor; Richard Flagan, NAE, California Institute of Technology; Rebecca Haffenden, Argonne National Laboratory; Thom Hodgson, NAE, North Carolina State University; Murray Glenn Lord, The Dow Chemical Company; William Ward, NAE, GE Corporate Research and Development (retired)

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