REMEDIAL ACTIONS FOR MIXED CHEMICAL/RADIOACTIVE WASTES AT THE COLONIE INTERIM STORAGE SITE

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ABSTRACT

Under the jurisdiction of the Formerly Utilized Sites Remedial Action Program (FUSRAP), the Department of Energy (DOE) assumed ownership of a uranium processing facility in Colonie, New York. Under FUSRAP, DOE is responsible for identifying, evaluating, and decontaminating sites used during the early years of the nation's atomic energy program or from commercial operations that Congress has mandated DOE to remedy. The former National Lead Industries facility was designated for remedial action by Congress in the 1984 Energy and Water Appropriations Act, and is now called the Colonie Interim Storage Site (CISS). The facility was used to produce counterweights, shielding, and penetrator munitions from depleted uranium metal. The facility included reduction furnaces, machining equipment, rolling mills, and electroplating baths.

Bechtel National, Inc. (BNI) is the Project Management Contractor for DOE, and is responsible to DOE for conducting remedial action at CISS. This paper describes the selection of the technical approach and development of work plans in general, and gives excerpts from a specific work plan developed by BNI to treat mixed chemical/radioactive wastes left at CISS. Although 10 work plans have been developed to date, this paper describes the destruction of sodium cyanide in electroplating baths used for plating uranium products with cadmium. A total of 4,294 liters of electroplating solution averaging 1.0 molar cyanide and 90 nCi/liter uranium were treated. The treatment method was oxidation with calcium hypochlorite.

As a result of this work, acutely hazardous mixed waste was converted to a uranium contaminated heavy metal sludge. The sludges were solidified with portland cement and sodium silicate. A total of forty, 209-liter drums of solidified waste resulted from this work.

INTRODUCTION

A significant aspect of the remedial action work associated with decontaminating and decommissioning former radioactive material processing facilities includes the treatment of residual waste streams. Typically, these wastes have three characteristics:

- They are mixed radioactive and chemically hazardous wastes.
- The volume of waste is small and finite since the facility is no longer operating.
- The wastes contain a variety of components which are not associated with the original operating process.

This paper also illustrates the method used to select decontamination techniques and to develop work plans for the treatment of these kinds of waste streams.

TECHNICAL APPROACH

There are four major considerations for each work plan: cost, health and safety, waste hazard reduction/elimination, volume reduction, and waste stabilization. Proven technologies and bench scale testing were used to develop empirically based estimates of operating parameters and to demonstrate the effectiveness of the treatment methods. Upon completion of the work, the plans were revised to formally document the work.

The technical approach used to address mixed waste found at CISS consists of seven steps designed to efficiently develop effective treatment methods. The major steps of the process are:

- Definition of problem
- Selection of method
- Bench scale testing
- Work plan generation
- Peer and management review

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- Field implementation
- Documentation

The first step in developing each work plan is defining the scope of work. During this process, goals are identified. Ten work plans resulted from identifying 10 discrete scopes of work.

After defining the problem, the second step is to select a potential method to treat the wastes. Preference is given to methods that are industry standard techniques and have been used in a wide variety of situations. The purpose is to minimize the time necessary for method development and startup. Additional considerations included health and safety, equipment configuration, final product, and cost.

The third step is bench scale testing. The bench scale testing is necessary to demonstrate that the selected method is viable for the waste streams to be treated. It was especially important to collect data that could be used to estimate full scale operating parameters.

After bench scale tests have been successfully conducted and sufficient data have been collected regarding operating conditions, the fourth step is to develop a written work plan. The work plans typically include the following elements:

- Introduction
- Waste description
- Method of treatment
- Operations considerations
- Equipment configuration
- Process operation steps
- Contingency methods
- Evaluation of risk
- Health and safety
- Quality assurance
- Bench scale results and calculations

The fifth step is the review of a draft work plan. Reviewers generally include engineers, health physicists, industrial hygienists, and managers. The responsibility of each reviewer is to comment on their areas of expertise and to evaluate whether the work can be performed as it is described in the work plan. Additionally, reviewers may comment on the need for a Quality Assurance Assessment (QAA). This is a formal process that evaluates the probability and consequences of failure of the work. In the event that a QAA is deemed necessary, it is appended to the work plan. The completed work plan is signed off by the author, a checker, a supervisor, and the project engineer, and is ready for implementation.

The sixth step is to perform the field operation in accordance with the work plan. The approach includes checklists that are based on the process operation steps. Each iteration of the process has its own checklist that is signed-off by the operator. BNI's experience is that checklists are very helpful in reducing human error. The authority to change the operation is typically assigned in the work plan. This approach permits for real-time decision making in the field and criteria that, if exceeded, cause the cessation of work.

When the operation is complete, the seventh step is to revise the plan to include changes initiated during field implementation. Work plans are revised by the cognizant field personnel to reflect how the work was actually conducted. Process checklists are appended to the work plan to provide documentation of the final results. The work plan is signed off and issued "as-built."

EXAMPLE

Work Plan for Cyanide Destruction

The problem addressed by this work plan was to disposition 4,294 liters of cyanide plating wastes left from a cadmium plating operation. The wastes averages 1.0 mole/liter of cyanide and 90 nCi/liter of uranium. The scope of this work plan was to destroy the cyanide and produce a stable product that could be solidified as a step toward eventual disposal.

The following excerpts from the work plan show the selection of method, bench scale results, evaluation of risk, and a copy of the operating process checklist used during the field operation (Fig. 1).

Method of Treatment

The method of treatment for the cyanide solutions was selected from Pollution Control in Metal Finishing by M. R. Watson (1973, 1st Ed.). Of the several methods for cyanide destruction available, reaction with calcium hypochlorite is the method of choice. The theoretical reaction is given in Eq. (1):

$$4NaCN + 5Ca(OCl)_2 + 2H_2O \rightarrow 2N_2 + 2Ca(HCO_3)_2 + 3CaCl_2 + 4NaCl \quad (1)$$

This process was selected because:

- Destruction of cyanide with this method results in a minimal increase in total waste volume.
- $Ca(OCl)_2$ is a readily available commercial chemical.
- Handling and metering $Ca(OCl)_2$ is relatively simple and non-hazardous.
- The reaction can be operated as a batch process which simplifies equipment requirements.

Batch No. ____________

____ 1. Set an empty 55 gallon drum in the water jacket.
____ 2. Clamp mixer and drum in place.
____ 3. Pump CN^- solution into the drum.
(1" = 1.65 gallons) Total Amount = ____________
____ 4. Add 1.35 lbs of NaOH per gallon of CN^- solution.
Amount = ____________
____ 5. Check pH and temperature probes.
____ 6. Clamp probes in place.
____ 7. Start Water flow in cooling jacket and check flow rate.
Flow Rate = ____________
____ 8. Start mixer.
____ 9. Start ventilation fan.
____ 10. Check operation of HCN monitor.
____ 11. Start screw feeder.
Additional Rate = ____________
____ 12. Add 2.75 lbs $Ca(OCl)_2$ per gallon of CN^- solution.
____ 13. At the halfway point of the batch destruction, check the screw feeder calibration. Rate = ____________
____ 14. After $Ca(OCl)_2$ addition is completed, stop cooling water when temperature starts to drop.
____ 15. Remove mixer and clamp.
____ 16. Clamp the lid with a drum sling.
____ 17. Remove the from with a drum sling.
____ 18. Pump water from cooling jacket.

Comments:

____________ Operator's Signature ____________ Date

Fig. 1. Process Checklist.

Treatment by gas chlorination was not chosen because chlorine gas is hazardous and the process requires sophisticated equipment.

Sodium hypochlorite (NaOCl) is less preferred because the process will result in a larger increase in volume. NaOCl will be used to rinse bulk storage tanks after they have been emptied.

Operational Considerations

Bench scale evaluations of the process have been performed using a volumetric screw feeder and a laboratory scale mixer. A fume hood and air pump were used to determine the off-gassing characteristics of the reaction with regard to HCN and Cl_2. The purpose of this configuration was to mimic the anticipated full scale equipment with regard to $Ca(OCl)_2$ addition and mixing.

Results of the bench scale tests were as follows:

1. The destruction of CN^- can be accomplished without generating HCN gas.

2. The means for controlling HCN off-gassing is to add NaOH to the cyanide solutions, prior to reaction, in an amount sufficient to maintain an elevated pH.

3. Cl_2 fuming is also controlled by adding NaOH.

4. The amount of NaOH required is related to the rate of $Ca(OCl)_2$ addition.

5. At a $Ca(OCl)_2$ addition rate of 3.56 gm/l/min, 160 gm/l of NaOH will prevent HCN generation and minimize Cl_2 off-gassing.

6. If insufficient NaOH is present, the Cl_2 will fume before HCN gas is generated.

7. Cl_2 is visible at low concentrations and detectable with Draeger tubes.

8. Fuming can be stopped immediately by adding NaOH.

9. Cyanide destruction with $Ca(OCl)_2$ is highly exothermic, (approximately 200 Kcal for CN^- or $Ca(OCl)_2$/gm-mole).

10. Reaction temperature was allowed to exceed 100°C and boil over the reaction vessel. No off gassing occurred under these conditions.

11. Given the amount of heat generated by the reaction, a cooling mechanism for the reaction vessel is necessary.

12. Volume increase is between 20 and 33 percent depending upon whether NaOH pellets can be used dry or if they must be dissolved in water at 50 percent weight/weight.

EVALUATION OF RISK

Hydrogen Cyanide

Risk of occupational and environmental exposure to HCN gas is directly related to the pH of the cyanide solution during destruction. When the hydroxyl radical (OH^{-}) is present in sufficient quantity, the destruction of CN^{-} can be accomplished without off-gassing HCN.

The process described in this work plan has three independent procedural and equipment factors that are designed to prevent releases of HCN:

1. HCN formation is prevented by the presence of OH^{-}, (pH > 10) the initial condition of the plating wastes is pH >14. During destruction of CN^{-} with $Ca(OCL)_2$ some OH^{-} is consumed. Bench scale tests have been performed to determine the amount of NaOH per liter that will prevent off-gassing HCN. This amount of NaOH will be added to each batch prior to adding $Ca(OCl)_2$.

2. The batch process is monitored with redundant pH instruments. The initial concentration of OH- is greater than 1 molar (pH > 14). If the pH reading of either meter drops below 14 during operation, $Ca(OCl)_2$ addition can be stopped and liquid NaOH added (50 percent NaOH solution will be kept near the work area for this purpose). Any equipment malfunction will be resolved before the batch is continued.

3. A continuous HCN air monitor operates in the vicinity of the batch and downstream of the ventilation fan. The monitor can detect HCN at 1 ppm and is set to alarm at 10 ppm (occupational health level).

Chlorine Gas

During bench scale operations, some off gassing of chlorine was observed. The quantity of gas generated can be controlled by the amount of NaOH in the reaction vessel. The amount of NaOH to be added to each batch is based on controlling both HCN and Cl_2. However, there will be continuous low level generation of Cl_2 in the reaction vessel. Calculations show that with continuous ventilation under worst operating conditions, the chlorine concentration at the property line of the facility would be below 0.1 percent of the occupational standard.

Uranium

Exposure of the environment to uranium is possible in the event of the batch reaction vessel boiling over into the cooling water jacket. To prevent this, the outlet cooling water will flow into a 760-liter vessel and then be pumped out to the environment. If the reaction vessel does boil over, all of the cooling water will be contained. Any contaminated cooling water will be put in barrels and tested for CN^{-} and uranium. Disposal options will then be evaluated.

CONCLUSIONS

From the approach used to plan and conduct mixed waste remedial action at the CISS, the following conclusions can be drawn:

- Using standard industry methods reduces the time and effort associated with configuring elaborate or sophisticated equipment for short-term operations.
- Bench scale testing empirically demonstrates the viability of the proposed approach and provides data on operating parameters necessary to implement the method on a larger scale.
- Interdisciplinary and management reviews evaluates the viability of the approach and the procedures of the work plan.
- Field implementation checklists aid in ensuring that the procedures developed in the work plan are followed, and reduce the opportunity for human error.
- Revising the work plans to reflect actual conditions encountered during implementation of the plan ensures that similar work can be conducted without redeveloping the work procedures.