HIGH-LEVEL WASTE SOLIDIFICATION OFF-GAS CLEANUP TECHNOLOGY

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INTRODUCTION

As technology for the solidification of the high-level wastes grows, it becomes more and more evident that a major portion of any solidification system will be the process off-gas cleanup equipment. Since the off-gas cleanup system plays such an important role in the solidification system, it is critical that the necessary off-gas cleanup technology be available when required. A variety of types of waste forms and solidification processes are being developed in the United States and abroad; many of the solidification processes are described in Alternatives for Waste Treatment.[1] Off-gas processing systems are being developed along with most of the solidification processes. An extensive review of off-gas cleanup methodology and decontamination factors can be found in the literature.[2]

With a number of waste solidification facilities around the world in operation, it can be shown that existing technology can satisfy the present requirements for off-gas control. However, a number of areas within the technology base could be improved. Fundamental as well as verification studies are needed to bring about the improvements. This brief overview is intended to be a basis for a discussion of the needs and problems existing in the technology. Since it is generally agreed that the most advanced

a Work supported by the U. S. Dept. of Energy under Contract EY-76-C-06-1830 with Pacific Northwest Laboratory.

solidification process is vitrification, discussion here will primarily center around the off-gas problems related to vitrification.

CURRENT TECHNOLOGY

The majority of off-gas cleanup systems in use today are similar to the system depicted in Fig. 1. The function of the off-

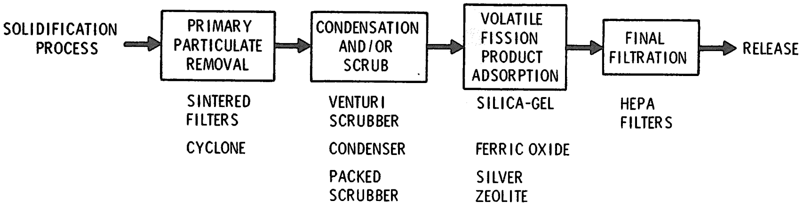

Fig. 1. Process Off-Gas General Flowsheet and Hardware

gas system is to remove particulates, volatile fission products and hazardous components (non-fission products) from the gas stream. This is accomplished in four basic steps. The first step is the removal of primary particulates using sintered-metal filters or cyclones. By far, the majority of the solids are removed from the gas stream at this point.

Following primary particulate removal, water, acids and fission products are removed by condensation and scrubbing. Acid can be recovered in this step and hazardous materials, such as nitrogen oxides, can be controlled. The equipment used here includes venturi and packed scrubbers, various condensers, and other gas-liquid contacters. The third step is the adsorption of volatile and semi-volatile fission products. Adsorption can be used as a "polishing" step for the other cleanup steps, or it can be used for primary volatile control as in the case of iodine. In general, silica gel or ferric oxide is used for the semi-volatile metals and silver zeolites for iodine. The final step in the off-gas cleanup system is again filtration. Before gases are released, high-efficiency particulate air filters remove the small solids that pass through the earlier cleanup steps and those that are re-entrained in the process.

PROBLEM AREAS IN OFF-GAS CLEANUP TECHNOLOGY

The major problem areas in off-gas cleanup technology are:

- volatile fission product losses and control
- volatile nonfission product losses and control
- particulate generation and control
- process off-gas treatment hardware efficiency
- effects of various solidification processes.

Each of these problem areas is discussed briefly below.

Controlling Volatile Fission Products

The major problems related to volatile fission products are:

- volatility in solidification processes
- characterization of volatile forms
- behavior in process off-gas system
- removal efficiency by various off-gas system components
- effects on off-gas system components.

The volatile fission products of primary concern are ruthenium, cesium, technetium, selenium, tellurium, antimony and iodine. The conduct of the fission products in most solidification systems is not generally understood. Studies are required to determine the volatility and form of fission products and their behavior in process off-gas systems. Determination of volatile fission product removal efficiencies is needed to allow selection of individual process off-gas equipment pieces.

Controlling Other Volatile Species

The concerns in the area of volatile nonfission products are the same as for volatile fission products. Studies are needed to determine how much material will volatilize from a solidification process, the form in which it will volatilize, and how it will behave in the off-gas system. Species of primary concern are mercury, fluorides and organics. Mercury will volatilize in nearly all of the high-temperature processes, such as vitrification. The exact form in which mercury will volatilize will depend on the other constituents present in the waste and the operating conditions during processing. It is expected that in the vitrification process nearly 100% of the mercury will volatilize to the off-gas system.

Wastes containing fluoride pose a different problem for the process off-gas system. A small percentage of the fluoride compounds in the waste will probably volatilize and when taken into solution in an aqueous-contacting off-gas system may cause corrosion problems and affect adsorbers. The behavior of organics in the solidification process and in the process off-gas system is not well known. It must be assumed that some portion of the organics will pass to the off-gas system where the potential for problems, such as poisoning adsorbent beds, exists.

Particulate Control

Although the decontamination factors for solids for most types of process off-gas equipment are fairly well known, processing of high-level wastes poses new problems. For example, both ruthenuim and mercury are unstable in their gaseous form in the off-gas system and will form particulate matter at various points in the off-gas train. Studies are needed to determine at what points in the off-gas system this transformation will take place and how it is related to the concentration of various constituents in the off-gas stream.

Solidification Process Analysis

A variety of solidification processes are being investigated today. Studies are needed to determine the off-gas related problems generated by each of the individual processes and to find the solutions to those problems. A specific example is the possible problem of ruthenium volatilization from the liquid-fed, ceramic-melter glass process. Due to the long feed residence time and the possibility of high acid and nitrate content, the potential for high ruthenium volatilization exists. Initial tests at Pacific Northwest Laboratory [3] have shown that ruthenium volatilization from the ceramic melter may be high, but that feed denitration can be used to control ruthenium losses. A variety of methods for denitration, such as batch feed, continuous in-calciner and continuous in-melter denitration, have been suggested for use. Testing should be completed to determine the amount of volatility suppression possible and the effects of denitration on the operation of the off-gas system. Potential off-gas problems also exist with the synthetic mineral waste form and the titanate, cermet and matrix-encapsulated waste processes. Unanswered questions relating to volatility and solids entrainment exist for nearly all of these processes.

Process Off-Gas Hardware

Needs in the area of process off-gas control hardware are:

- the operational optimization of sintered filters
- the development of ruthenium adsorbers
- NO_x reduction testing
- determination of effects of integration of off-gas components
- the improvement of off-gas sampling and measurement techniques.

A number of solidification processes use sintered-metal filter for the separation of gases from entrained solids. Studies are needed in the area of operational optimization of these filters. Filter blowback, as well as physical configuration, should be arranged to minimize the penetration of solids through the filters.

A variety of materials could be used to adsorb volatile ruthenium from the off-gas stream. Silica-gel is the adsorbent most commonly used today. However, while silica-gel provides sufficient decontamination factors, it causes a final disposal problem. Ferric oxide is being used in place of silica-gel; although ferric oxide is not regenerable, the use of ferric oxide may allow the disposal of adsorbed ruthenium by incorporation in the high-level waste glass. Since ferric oxide adsorbers can operate at higher temperatures, they could be used at the front end of the off-gas system. Studies are needed to optimize the use of the ferric oxide; optimal physical configuration, flow rates, tempertures, etc. need to be determined. Since the potential for revolatilization of ruthenium exists, the disposal of loaded ferric oxide in the waste product also needs to be investigated.

In solidification processes in which there is a high nitrogen oxides content in the off-gas stream, an NO_x reducer may be used to reduce the nitrogen oxides to nitrogen or N_2O. In addition to reducing the NO_x, the reducer may also be used as a volatile fission product adsorber. Studies are needed to determine volatile fission product decontamination factors for NO_x reducers and the effect of the fission products on the operation of the reducer.

Integration of individual process off-gas equipment pieces may cause changes in the operation of some of the individual pieces. An area needing study is the effect of single component failure on overall off-gas system efficiency. The failure of a single component in an off-gas train may lower the overall decontamination factor to the point that the system could not operate.

Improved methods of off-gas sampling are needed to accurately characterize off gases from high-level solidification processes. The primary problem lies in the difficulty in obtaining and measuring a sample of relatively small activity in a highly radioactive hot cell or cave environment. The development of on-line, real time measurement methods is needed.

CONCLUSIONS

The technology for solidification process off-gas control does exist, but studies are needed to meet future process changes as well as to improve the control available today.

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