

**DWPF Vitrification Safety Issues**

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## DWPF Vitrification Safety Issues

**Abstract:** High level waste volume minimization currently requires addition of organic compounds to precipitate Cs from the high volume of supernate. In addition, the alkaline nature of the waste requires pretreatment of the waste prior to introduction to the melter which then calcines and vitrifies simultaneously. These pretreatment operations in the Defense Waste Processing facility (DWPF) can release hydrogen, benzene, ammonia, and carbon monoxide which could, under upset conditions, result in flammable mixtures. The design of the facility has accounted for accidents of this nature and provides defense in depth for prevention. Use of the DWPF process for direct vitrification of  $\text{PuO}_2$  is not recommended due to the significant required design changes to ensure criticality safety. However, cans of  $\text{PuO}_2$  in ceramic matrix which are subsequently placed in a DWPF canister prior to high level waste glass being poured appears to introduce no new significant safety issues.

**Background:** Forty years of nuclear materials production at the Savannah River Site has generated over 300 million liters of aqueous radioactive waste to date. This waste has been primarily generated from the two fuel reprocessing facilities as fission products from reactor irradiations. The current volume of waste is less than half the above due to processing through evaporators to remove excess non-radioactive water. The total activity stored in the tanks is over 600 million Curies ( $2.2 \times 10^{15}\text{Bq}$ ).

Waste generated from operations in the reprocessing facilities was transferred to carbon steel underground storage tanks. Addition of NaOH minimized tank corrosion by making the waste strongly alkaline. Over time, the waste in the tanks physically separated into two components. A dense sludge consisting of metal hydroxides and hydrated metal oxides (primarily Fe, Al, Mn and actinides) settled to the bottom. A supernate containing soluble salts such as Cs floated on top of the sludge. Because each phase contained highly radioactive materials, the final waste dispositioning process was required to vitrify both supernate and sludge.

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**Waste Pretreatment:** This decision was made to treat each phase separately. The sludge would be jetted from the bottom of the tank, treated with caustic to remove the Al solids, washed with inhibited alkaline water and the remaining sludge transferred directly to the DWPF. The wash water would be processed at the low level waste saltstone facility.

The supernate would be transferred to a dedicated tank and decontaminated by adding tetraphenylborate causing the Cs, K & Na to precipitate out of solution. Also, sodium titanate would be added to adsorb Sr, U and Pu. This mixture of solids would then be concentrated by filtration forming a precipitate slurry and low level waste solution. The solution would be processed into grout at the Saltstone facility while the precipitate slurry would be transferred to the DWPF.

**DWPF Processing:** Due to the alkaline nature of the SRS waste, directly calcining the material is impractical. Therefore, the waste material must be chemically processed in several steps prior to being added to the melter in which calcination and vitrification is performed in one vessel. Each step of the process was analyzed during the design process to determine required safety features. Hazards during normal and accident situations are identified and if potential consequences are too high, engineered safety equipment is designed into the facility.

The precipitate slurry transferred to the DWPF may have nitrite composition which exceed levels which are compatible with the remainder of the process. Acceptable nitrite levels are assured by processing the precipitate through the Late Wash Facility. While the slurry is being processed, benzene and hydrogen are being released from normal tetraphenylborate decomposition and radiolysis caused by the incumbent radionuclides. If not controlled, these flammable gases could reach concentration levels in the vapor space which could support combustion or deflagration. Prevention of such an occurrence is assured by provision of a safety class nitrogen purge system which maintains the oxygen level at a low enough percentage to preclude combustion.

Excess organics are contained in the precipitate slurry transferred from the Late Wash Facility. These organics must be removed prior to vitrification in the 1150°C melter. The Precipitate Reactor receives the

nitrite balanced slurry from the Late Wash Facility where it is heated and chemically treated to cause the release of benzene which is unavoidably accompanied by hydrogen. This benzene is transferred to another system to be purified and ultimately combusted. However, during the processing in the Precipitate Reactor, a continuous CO<sub>2</sub> purge is added to assure low oxygen concentrations in the vapor space and prevent deflagrable mixtures from forming.

The next two vessels in the process are the Sludge Receipt and Adjustment Tank (SRAT) and the Slurry Mix-Evaporator (SME). The sludge from the waste tanks enters the DWPF process at the SRAT. The role of these vessels is to neutralize the sludge, remove Hg, adjust pH to improve rheology and add the glass frit. The safety hazards inherent in these processes are ammonia gas which will form ammonium nitrate and condense in the ventilation system. Safety systems added to these processes include air/nitrogen purges to remove benzene and hydrogen and ammonia scrubbers to remove ammonia from the offgas preventing the formation of ammonium nitrate.

Finally, this mixture arrives at the melter where the waste is vitrified. In the melter, organic impurities are released which have been carried over from earlier processing and the gasses of hydrogen and carbon monoxide are generated. The temperature and air flow into the melter are designed to provide complete combustion of the gases before they reach the offgas system. If the design temperatures and air flows are not met, there are safety class interlocks which stop the feed entering the melter.

**Pu Disposition:** With regard to using the DWPF for vitrifying PuO<sub>2</sub>, it should be noted that the Pu-239 content in the design basis waste glass is only 1X10<sup>-2</sup> wt%. This provides for the trace Pu that is within the waste. A canister of waste glass therefore contains less than 200g Pu-239 and is surrounded by integral neutron poisons such as Fe and Mn. For this reason, DWPF process is inherently safe from a criticality perspective.

If the DWPF was to be used to vitrify PuO<sub>2</sub> directly (i.e., no prior process to make PuO<sub>2</sub> frit), the PuO<sub>2</sub> would presumably be added to the process in the SME. Economic feasibility of the process would require addition of PuO<sub>2</sub> in the tens of kilogram quantities in a batch. Masses of this magnitude are not inherently

safe and the vessel is not geometrically favorable for preventing criticality. Therefore, the current design could not assure criticality safety due to the inability to assure homogeneous mixing and the potential for Pu to collect over time to form a critical mass.

The situation is similar for the melter. The melter would contain over 100kg of Pu and is not designed for inherent criticality safety with that mass amount. Also, the ventilation system was not designed for the possibility of Pu offgassing. Major redesign of the DWPF vessels and ventilation system would be required.

Another risk that is exacerbated if  $\text{PuO}_2$  powder is introduced is that of fire. Clearly the use of cold chemicals, the presence of electrical cabling and the generation of flammable gases leads to a defined fire risk. Unless buildings are designed with fire propagation as a design parameter or combustibles are kept at very low levels, fires can spread to areas where radioactive materials are present potentially resulting in a thermal, elevated release from the facility. If  $\text{PuO}_2$  is introduced as a fine powder or stored in sealed cans, care must be taken to assure release due to a fire is prevented. The fine powder can be made airborne if disturbed and the storage cans may rupture causing a significant release. The potential source term for the DWPF would increase dramatically if  $\text{PuO}_2$  was present.

However, an alternative process being discussed is called the Can-In-Canister (CIC) concept. In a facility separate from the DWPF, the  $\text{PuO}_2$  would be immobilized in a ceramic matrix. This form would then be placed in a stainless steel can with dimensions much smaller than a DWPF canister. Approximately twenty of these cans would be placed in a rack which is then inserted into an empty DWPF canister. The canister would then follow its design path which is to be filled with molten glass thus, encasing the smaller cans within the highly radioactive waste glass.

This process, if the cans are designed properly, would introduce no new safety issues in the DWPF. There is no accident considered which could release  $\text{PuO}_2$  from the cans in a manner which could harm the workers or public. The separate facility which creates the  $\text{PuO}_2$  ceramic must deal with several hazards including  $\text{PuO}_2$  powder and criticality.

**STATUS:** To date, DWPF has rendered immobile over 1,000,000 liters of sludge in over 1.4 million kilograms of glass. Observed gas generation (hydrogen and ammonia) have been within the anticipated ranges. No precipitate slurry has been processed to date so significant organic releases have not been observed. Currently, alternative processes are being evaluated for treating the supernate as higher than expected benzene generation rates were observed during initial processing.