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Research on the Safety of High Level Liquid Waste Storage in China

Zhang JIANGANG*, Tang RONGYAO, Zhao BIN, Wang XUEXIN
China Institute for Radiation Protection

Characteristics of high-level liquid waste (HLLW) in China were investigated and safe handing of HLLW was discussed, especially with emphasis on accumulation and release of hydrogen, chemical hazards of organics and heat-up. Several recommendations concerning human factor and operational management were proposed for the achievement of safe management of HLLW.

KEYWORDS: high level liquid waste, storage, safety,

I. Introduction

In 1957, the explosion of a HLLW tank occurred in former U.S.S.R.[1] It was said to be the second severe accident since the beginning of the nuclear industry. The accident was caused by the heat-up of the HLLW system. The HLLW became totally dried out because of losing cooling water. An explosion of a mixture of nitrate and acetate occured. Since the accident being revealed in 1990's, A considerable attention has been paid on the safety in storage of HLLW in many countries.

The study concerning the mechanism and possibility of potential severe accidents of HLLW tanks in China was conducted in China Institute for Radiation Protection (CIRP) in the period of 1996 to 2000. Composition of the HLLW is a mixture of gas and aerosol, organic phase, aqueous phase and sediment. This paper mainly dealt with the problems of the production and accumulation of hydrogen, hazards of organic chemicals and heat-up.

II. Characteristics of HLLW tanks in China

The HLLW in China is mainly produced by the process of Plutonium-Uranium Reduction Extraction (Purex) as a result of reprocessing of nuclear spent fuel. The storage tanks were made of stainless steel[2,3]. The old type of tanks built in 1970's are of single-shell type with a stainless tray. The new types built in 1990's are of double-shell stainless tanks with stirring systems. There are two new types of tanks with wall thickness of 8 cm or 10 cm. The concentration factor of HLLW is about 40. The thickness of sediment is estimated not to exceed 50 cm as the sample collection has shown.

There has been no phenomenon of induration to be found in sediment, as indicated in sampling collection. The safety functions of such storage tanks include cooling, ventilation, containment, shielding and transferring. Temperature of HLLW is controlled below 60 ℃. The tank inner pressure is set at 150 Pa. Concentration of hydrogen gas is kept below 0.5% (V: volume percentage) . Leakage of HLLW can be detected by using a aerosol monitoring system.

*Corresponding author, Tel. +86-351-2202410,
Fax. +86-351-7020407, E-mail: zhangjiangang@163.net

III. Hydrogen in HLLW tanks

1. Mechanism of hydrogen production

The hydrogen in tanks is produced through three mechanisms[4]: radiolysis, thermolysis, and corrosion. Radiolysis occurs in the liquid phase. Thermolysis means the reaction between organic materials, sodium nitrate and aluminum salt. The amount of hydrogen arising from corrosion is dependent on the contact area between liquid waste and the tank, the tank material and the pH of the waste.

2. Accumulation of the hydrogen

The ventilation system is designed to keep the hydrogen concentration in HLLW tanks less than 0.5% (V), and until now "Burp" phenomena (a phenomenon that the bulk of hydrogen may release suddenly) have not been found yet, so there is little chance of hydrogen burning under the normal condition of ventilation.

The research work of Hanford shows that there exists N_2O in HLLW tanks[2]. The percentage range of hydrogen volume under accidents of deflagration and detonation changes from 4%-72% (V: volume percentage) to 3%-84% (V: volume percentage) because of the existence of N_2O. For a certain tank, our calculation result shows that the time span for hydrogen changing from 0.5%(V) to 3% (V)(lower limit of deflagration) is 9 hours under the condition of ventilation failure, the emergency response system failure and the breath(a passive ventilation channel) failure. The breath with the breath rate of 60 liter/min starts after ventilation failure, the time span will be 11.14 hours. If using the less conservative hydrogen production rate, calculated with Hanford's empirical formula, the time span will be 39.8 hours, which means that there is more response time for workers to fix ventilation system and to avoid hydrogen burning accident.

3. Tank pressure from hydrogen burning

The existence of N_2O may lead to an increase in the energy released from hydrogen-air reaction by 34% for the same volume hydrogen. Our analysis shows that the pressure in tank will increase 0.15 MPa when hydrogen burning occurs under the condition of adiabatic isochoric complete combustion at the concentration 5% (V).

Under the condition of hydrogen being ignited with the concentration up to 42%(V), detonation may probably happen. The increased pressure resulting from detonation would be larger than that from adiabatic isochoric complete combustion (AICC). The local peak pressure can be 35 times higher than that under the normal condition.

IV. Organic constituents in HLLW tanks

1. Organic constituents in HLLW and their hazards

There are three categories of chemical hazards besides flammable and poisonous gas[6]:

First, the organic solvent might burn. There exist a small amount of organic solvent in HLLW in China, including tributyl phosphate (TBP), normal paraffin hydrocarbon (NPH) and degradation products from Purex process.

Second, the organics, organic complex and degradation products may come into reaction with sodium nitrate. The work of cesium and strontium extraction from HLLW tank in China has never been found, therefore there are little organic chemicals such as citrate and acetate in these tanks.

Third, Hanford study shows that the ferrocyanide may come into reaction with nitrates at high temperature. However, there are no such hazardous chemicals in HLLW tanks of China because ferrocyanide was introduced in the process of cesium extraction.

Therefore, the research work was mainly focused on the organic solvent combustion and the reaction between organic chemicals and nitrates.

2. Organic solvent combustion accident

The volume of organic solvent is small comparing with the total HLLW in the tanks. The thickest organic solvent layer is about 1 cm. For past many years of storage, most of NPH volatilized. The remaining organic compounds are mainly TBP and the degradation products. TBP, which is difficult to be ignited can only be ignited by intense and sustainable fire. Furthermore, the burning of TBP is not as intense as hydrogen burning. TBP, generally in the state of liquid, can not be ignited until being vaporized in a large volume.

Suppose a tank is airtight and adiabatic and the reaction stops when oxygen is exhausted, the results of calculation shows that the pressure may approach 0.996 MPa in the tank. However the real burning consequence is much smaller than that in the case of hydrogen burning.

3. Organic-Nitrate reactions

As indicated by Hanford study, the limit of acetate content was defined as 10% organic content calculated as sodium acetate, which corresponds to 3% total organic carbon (TOC). This is the present organic tanks watchlist criteria at Hanford. Under the condition of both the above-limit fuel concentration and the ignition source existence, the organics and nitrate may come into reaction.

The organic constituents in HLLW arising from radiolysis and thermolysis vary widely and are difficult to detect, while TOC is relatively easy to be measured. The organic constitutes in the tank can be classified as CH_2, CH_2O, CHO in terms of their features. When the weight percentage of water in HLLW is greater than 60.15%, 55.99% and 47.05% respectively, the three types of organics fail to sustain the reaction between organics and nitrate, regardless of the organics concentration. This kind of accident can be avoided because the weight percentage of water in HLLW of China is far greater than 60.15%.

On the other hand, even if the water of the system evaporate to dryness, the reaction will not be self-sustained when TOC is less than 0.25%.

V. Heat-up

The maximum temperature in HLLW is still less than 100 °C even when cooling and ventilation systems are in failure for two weeks, which has been indicated by the temperature distribution calculated using the computer code Heating 6.1[7] based on the following assumptions:

no convection in the 50-cm-thick sediment, adiabatic facility room wall, failure in cooling and ventilation systems, no account being taken of evaporation, heat radiation and chemical reaction.

VI. Preliminary conclusions:

Through the analysis above, we can see that the main problem of HLLW in China among hydrogen, organic, heat-up is from hydrogen. The possibility of potential accidents from the other two are comparatively smaller. The sudden release of bulk of gas (so-called "burp") has never been observed, then it is not difficult to avoid the hydrogen burning accidents. On the other hand, because of the possibly existence of N_2O, the consequence of hydrogen deflation or detonation would be severer than was predicted before.

Through the analysis of organics we can find that the organic solvent combustion accident unlikely happens. The hazard from organic-nitrate reaction would be also small, due to the HLLW storage situation in China. When the constitutes of the waste in the tanks are not known exactly, the effective way of avoiding organic-nitrate reaction is to control the temperature of HLLW, which could be done through the control of liquid level and/or cooling system.

Based on the conservative assumptions foregoing, the maximum temperature of HLLW calculated is less than 100 °C under the condition of cooling and ventilation system in failure for 2 weeks . The sampling and analysis show that at the sampling point the sludge is in movement, and there is no crust (or so-called salt cake) to be found. Thus, heat-up will not pose a big problem under the condition of HLLW in China. However, it is necessary to keep appropriate liquid level so as to avoid sediment accumulation。

VII. Recommendations on safety management

First, safety culture is very important. The experiences of nuclear industry from different countries show that the percentage of the accident caused by human factors is more than 50% on the whole. The severe accidents are closely related to human errors.

Second, the focal points of operational management for HLLW are to keep the normal liquid level, keeping the normal operation of ventilation system and emergency response system and to prevent fire. The operational experiences show that the probability of power loss is quite high in the plants. It is therefore important to maintain the extra power supply.

The safety analysis on HLLW storage needs a lot of work. With the research work going on, the safety aspects on HLLW will be understood further.

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