THE WOX PROCESS - NEW VOLUME REDUCTION TECHNOLOGY FOR REACTOR WASTE

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ABSTRACT

During 1984 to 1986 ASEA-ATOM has together with Vattenfall carried out tests of a wet oxidation process for volume reduction of spent organic ion exchange resins in both laboratory and pilot plant scale. ASEA-ATOM started the development of this process in 1983 in cooperation with EKA Nobel AB, a major manufacturer of the oxidizing agent hydrogen peroxide, who contributed with their knowledge about the specific chemistry regarding the hydrogen peroxide in the oxidation process. In 1984 a large amount of the laboratory experiments, both non-radioactive simulated tests and real tests with condensate cleanup resins, were carried out. These experiments resulted in the construction of a pilot plant, designed to treat batches of 100 kg dry resin.

Non-radioactive pilot plant tests were performed in the ASEA-ATOM laboratories and the hot tests were executed at the nuclear power plant at Forsmark in cooperation with Vattenfall. During the radioactive tests resins from the condensate cleanup system were used. The results from these tests have been most satisfactory regarding both the process, the equipment and the final product. Furthermore, during 1986 also some powdered resins from the Italian BWR-plant Caorso were treated with good results. The obtained volume reduction cement solidification a volume reduction factor of 15 can be achieved by the new WOX process.

INTRODUCTION

The strategy of the management of radioactive waste from nuclear power plant operation has gradually shifted over to an increased emphasis on volume reduction. The reasons may vary with the local conditions from one country to another and sometimes also between different sites within one country. A heavy influence would be the increasing cost of interim on-site storage and transportation as well as the problems of final disposal. One way of dealing with this problem is to reduce the volume of the produced waste by some sort of process or treatment. This is the idea behind the ASEA-ATOM Wet Oxidation Volume Reduction and Solidification System, which is named the WOX process.

The process is capable of reducing, to a large extent, the volume of different types of organic waste, e.g. spent ion exchange resins. In terms of total volume reduction at a nuclear power plant, the largest reduction will be achieved in the treatment of resins from a BWR plant, depending on the large amount of the spent resins generated from the condensate cleanup system.

The development of the WOX system is the result of a cooperation between Vattenfall, the operator of the Forsmark and Ringhals Nuclear Power Plants, the chemical industry represented by EKA Nobel AB and the nuclear power plant supplier ASEA-ATOM.

PROCESS PRINCIPLES

The WOX process utilizes hydrogen peroxide as the oxidizing agent for the decompositon of the resins. The specific feature of the WOX process is the technique for the treatment of the residual solution and this constitutes the basis for obtaining the high volume reduction factor.

When a mixed cation/anion exchange resin is decomposed, the residue will be a solution of sulfuric acid and a small amount of ammonium sulfate. The radioactive material will be in the form of particles and dissolved ions such as Co^{2+} and Cs^{+}. Prior to further treatment this solution is neutralized with for instance sodium hydroxide. The main component in the solution will then be sodium sulfate. The weight of the sodium sulfate will be in the order of 50% compared to the original weight of the dry resin. This means that a significant part of this waste consists of non-radioactive salts.

The common way of treating this liquid residue is by means of evaporation and final solidification of the concentrated salt solution in a suitable matrix. By this manner, radioactive as well as non-radioactive material will contribute to the final waste volume. In the WOX process the radioactive material will be separated from the sodium sulfate solution and only the radioactive part will be the subject of solidification and thus contribute to the final waste volume. The non-radioactive salt solution will be directed to the liquid discharge system of the power plant.

Thus an exceedingly high volume reduction can be obtained by treating the above mentioned waste in a WOX plant. The WOX process comprises the steps shown in Fig. 1.

In the pretreatment step the resin slurry is charged to the reaction vessel. If necessary, the dry content is adjusted to about 20-25% by weight. The pH value is then lowered by adding sulfuric acid. As the wet oxidation reaction requires a catalyst, ferric ions can be added in the form of ferric sulfate. The slurry is then heated to about 90°C.

During the wet oxidation step the hydrogen peroxide is continously pumped to the mixing zone of the vessel. The hydrogen peroxide is in the liquid form and is often used in the chemical industry. The main industrial application of the hydrogen peroxide is as a bleaching agent in the pulp industry.

The hydrocarbon matrix of the resin will be decomposed during this process step and oxidized to carbon dioxide and water. The non-radioactive carbon dioxide is released via the plant controlled area ventilation system.

As the oxidation process takes place at atmospheric pressure the reaction vessel does not have to be designed for overpressure.

The reaction is exothermic and the heat of reaction is sufficient to keep the temperature at the proper level. As the boiling temperature of the aqueous phase is slightly above 100°C, the temperature can not exceed this value. Thus the system is self-regulating.

After the completion of the oxidation step, the acidic mixture is neutralized by means of soidum hydroxide. Ferric hydroxide will precipitate and most other metal ions, such as the activated corrosion products, will be coprecipitated. Sodium sulfate will be the main product still being dissolved in the water. Furthermore, small quantities of some metal ions, such as cesium and strontium, will remain in the solution.

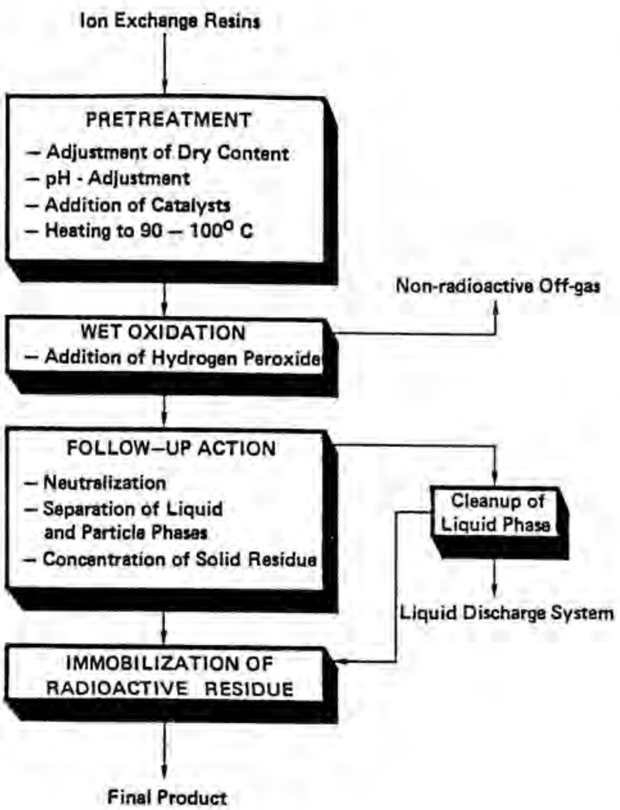

Fig. 1. WOX Process Principles.

The large amounts of non-radioactive salts in the solution, mostly sodium sulfate, must be separated from the solid radioactive material in order to obtain a high volume reduction factor. This is performed in the separation step by utilizing settling/decanting or filtration techniques. To ensure that the main part of the non-radioactive salts will be transferred to the clear liquid phase, the slurry is washed with fresh water. The concentrated radioactive waste slurry is then transferred to the solidification step and immobilized in a cement matrix according to the ASEA-ATOM solidification recipe and technology.

The liquid phase can either be released or, if it contains unacceptable amounts of cesium and strontium, be passed through ion exchange columns in a liquid phase cleanup step. The object of these columns is to selectively absorb these ions and neglect the predominant non-radioactive sodium ions. Adsorbents with this capability can be exemplified by zeolites, so called molecular sieves. Only a small part of the selective capacity of the column is consumed for each wet oxidation batch. When the entire column is spent, it is exchanged and the spent absorbent is taken to the solidification step.

The spent column material can be solidified either separately in a cement matrix or be mixed with the main part of the waste slurry prior to the solidification step.

The applications for a wet oxidation system are volume reduction of a variety of different organic waste materials. The main application for the WOX system is spent ion exchange resins which could be powdered or bead resins. Though both of these types can be decomposed during the wet oxidation procedure, the granular bead resins should be ground before fed to the reaction vessel in order to get a more economic utilization of the hydrogen peroxide.

The spent ion exchange resins can be devided into two waste categories, intermediate level resins and low level resins. The intermediate level resins are generated in, for instance, the pool water and the reactor water cleanup systems. One specific fact must be considered when treating this category in a volume reduction process. The reduction of the waste volume gives also as a consequence a concentration of the radioactivity. The result will be higher dose rates and if the dose rates were high already from the start, this must be taken into consideration for the further handling of the waste packages.

The predominant low level waste category generated is spent powdered resins from the condensate cleanup system at a BWR plant. This waste type has the physical and chemical properties in order to make it suitable for treatment in the WOX plant. Normally there will be no problems with further handling due to high dose rates. No grinding is required. As this type of spent resins is generated in large amounts at BWR plants it will certainly motivate the investment costs for installing a WOX plant.

TESTS WITH RESINS FROM FORSMARK NPP

The development of the WOX process started with a series of tests in laboratory scale. Based on the results of this small-scale tests a pilot plant was constructed and built in a scale about half the necessary size of a full-scale industrial unit. The pilot plant was then used for verification tests of the process and the equipment.

At first the pilot plant was erected at the ASEA-ATOM laboratories where non-radioactive tests were performed. Powdered ion exchange resins were treated in batches of 100 kg of dry material. The process behaved in the same manner in this large scale as in the laboratory tests. The reaction time for the wet oxidation step was about 5 hours.

In order to separate the liquid phase from the particles a settling/decanting technique was tested. The particles were allowed to settle in a conical tank and the supernatant liquid was pumped from the surface by a sond which has the capability of indicating the interface between the clear liquid and the settled phase. This process step is easy to operate and gives good results but is time-consuming.

After the completion of the non-radioactive tests the pilot plant, which was made of movable rack-mounted subunits, was transported to the radwaste treatment building at the Forsmark NPP for verification tests with actual radioactive condensate cleanup resins.

The wet oxidation process performed in the same manner as in the previous test runs. Phenomenons such as foaming could easily be controlled. No carry-over of radioactivity in the off-gas flow could be detected.

The precipitation step for separation of activated corrosion products from the residual liquid gave the same results as in the laboratory study. An over-all decontamination factor of 120 was achieved.

The separation step for cesium and strontium was tested with a zeolite for selective adsorption of cesium and sodium titanate for strontium. Each liter of these column materials proved to have the capability of cleaning several hundred liters of residual solution.

TESTS WITH RESINS FROM CAORSO NPP

This test run comprised the treatment of ten drums (standard 200 liters) with centrifugated spent ion exchange resins from the condensate cleanup system. This waste was generated during the start-up period of the Caorso BWR plant in Italy.

The test run was carried out with a slightly modified pilot plant. The settling/decanting devices were replaced by a crossflow microfiltration unit in order to enhance the capacity of the phase separation step. Ordinary static filtration is not possible for this specific medium but crossflow filtration gives good results. In this technique a high fluid velocity sweeps particles across the membrane surface. The high velocity minimizes the solid layer build-up and maintains a high permeate flux. The filtration unit consisted of a bundle of tubular membranes, where the crossflow motion was created by a large flux through the unit.

The result from the treatment of the ten drums in the WOX plant was one drum of cement solidified product. Based on this test run a volume utilization figure could be determined for the WOX process which is defined as the amount of initial dry resins in kilograms that ends up in one cubic meter of final solidified product. The amount of dry resins should be calculated as totally waterfree matter containing no internal moisture in the resin structure. The volume utilization figure will then be about 2 300 kg/m^3.

UPCOMING ACTIVITIES

Plans are made for additional process verification runs with condensate cleanup resins from Forsmark NPP. The aim is to find the best solutions for the final details in the process design so that a complete nuclear industry adapted concept could be present during 1987. One area of specific interest is the introduction of the latest generation of the cross-flow filters into the WOX process. Here the crossflow is generated by agitator blades rotating with speed over the flat membranes. By this technique developed by ASEA-ATOM, it is possible to concentrate the slurry to such a high degree of dry content that it will be directly suitable for cement solidification.

COMPARISON WITH OTHER SWEDISH RADWASTE TREATMENT SYSTEMS

In Sweden different techniques for the solidification of the bead and powdered resins and filter material are currently used. At the Oskarshamm and Ringhals nuclear power plants this type of waste is incorporated into cement with a conventional method. At the Barseback and Forsmark nuclear power plants resins are bituminized but different systems are used. In Barseback a thin film evaporator of the LUWA-type is used. In the Forsmark 1 plant the waste is dried with a drum dryer and mixed with bitumen. This process gives a volume utilization of about 500 kg per m^3. The Forsmark 3 plant dries the waste in a conical dryer with a planetary mixing device prior to mixing the waste with bitumen in a simular vessel. The achieved volume utilization with the latter ASEA-ATOM designed process is about 750 kg per m^3.

Further, the Forsmark 3 waste treatment plant can also be used with cement as solidification agent and the same conical dryer is used for drying and heat treatment of the waste before it is mixed with water, chemical additives and cement. The waste loading in the matrix with this ASEA-ATOM New Cement Process can be two to three times higher than the conventional cement process.

The volume reduction obtained when treating ion exchange resins in the WOX process can be demonstrated by the following example. A batch of ion exchange resins (cation/anion 2:1) with a dry content of 100 kg (calculated as totally waterfree material) is charged to the WOX system. After treatment in the described process the final cement solidified product will amount to 34 litres. In case the liquid phase has been treated in the zeolite-based column system, the final volume of the cement solidified spent adsorbent material will amount to about 10 litres. All together, 100 kg of dry material will then end up in a final waste volume of about 44 litres.

The volume utilization figure for this treatment process will then be in the order of 2.300 kg original dry resin per m^3 final solidified product. The equivalent figure for a conventional cement solidification system is about 150 kg/m^3. Consequently, the volume reduction factor achieved by the WOX process is in the order of 15 compared to conventional cement solidification.

Figure 2 below shows a volume utilization comparison for four of the mentioned Swedish solidification processes designed and constructed by ASEA-ATOM. The product volumes represents the final result after treatment and solidification according to the different methods, starting with 1 m^3 of slurry with a dry content of 200 kg powdered ion exchange resins. The WOX process is presented under the title "Cement High Volume Reduction".

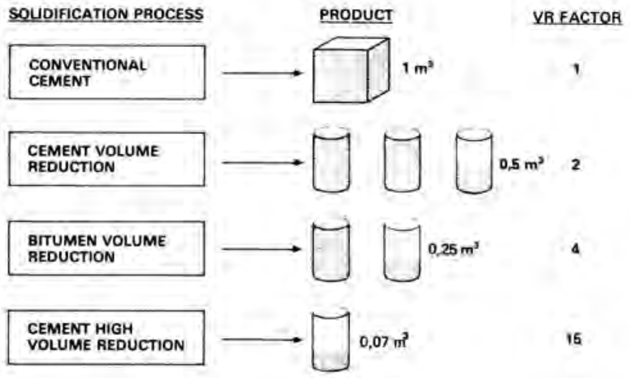

Fig. 2. Volume Reduction and Solidification Systems.

CONCLUSION

The WOX system has proved its ability to reduce the volume of radioactive organic waste efficiently. The main application is the spent ion exchange resins from the BWR condensate cleanup system due to the large amounts produced of this waste category.

The final product of the WOX process is characterized both by the stability of a cement solidified waste product and a large degree of volume reduction that is not usually associated will the cement solidification technique. The WOX process with therefore represent a unique combination of good product quality and volume reduction.