

CONDITIONING OF SPECIAL WASTE MATERIAL WITH THE FAVORIT VACUUM DRYING FACILITY

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The FAVORIT vacuum drying process for aqueous liquid waste and the related equipment was presented in detail at the EPRI Conference 1998. It was mentioned that the process, due to its specific features, is quite insensitive to the chemical properties of the raw waste to be processed.

This has been demonstrated by the treatment of two special waste types, namely

- phosphoric acid, and
- oxalate solutions.

INTRODUCTION - THE PROCESS

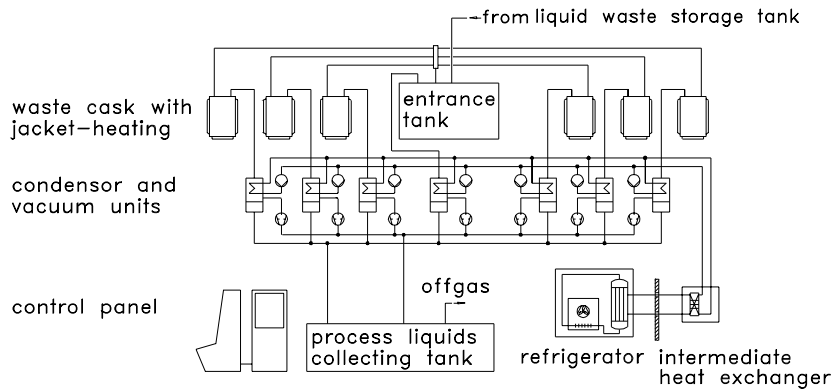
The FAVORIT process is a vacuum drying process for the treatment of aqueous liquid waste operating at low temperatures. The liquid waste is solidified through elimination of its water content. By this a volume reduction of the waste by a factor of 6 to 7 compared to the original raw waste volume can be achieved. By operation at low temperatures undesirable chemical reactions in the waste product can be avoided.

The use of volume reducing processes is of special importance when the conditioned waste products have to be stored in engineered interim stores due to lack of a final repository in a given country.

It has been reported last year, that in Germany a final repository in the former salt mine at Morsleben is available, which was believed - according to its operation license - to be ready to accept low-level radwaste till mid of 2000. In the meantime the situation has changed dramatically: Due to a court ruling on Sept. 25, 98 Morsleben is shut down. Due to a changed political situation, the two other repositories under development, the KONRAD mine for low and intermediate level waste, and the GORLEBEN salt mine for high level waste are under questioning.

So, for the time being, only engineered interim stores are available to accept radwaste in Germany.

A simplified flow diagram of the FAVORIT process is given in Fig. 1

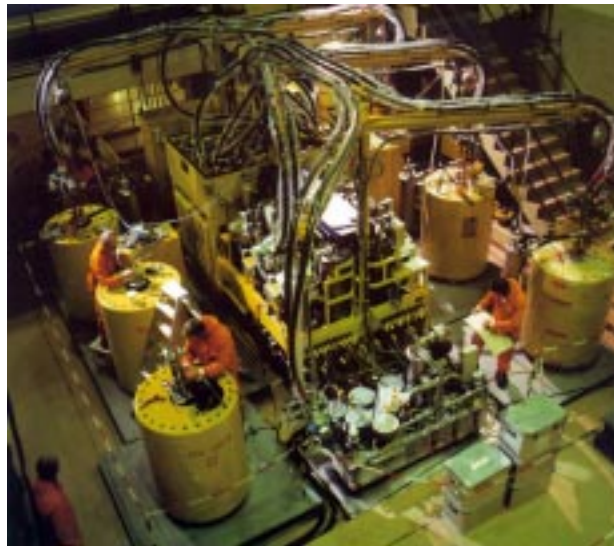


(Fig. 1: FAVORIT Process - Simplified Flow Diagramm)

showing the main components

- waste entrance tank
- waste containers with heating
- condenser and vacuum unit
- refrigeration system
- process liquids collecting tank

Fig. 2 shows the setup in a nuclear power station.



(Fig. 2: FAVORIT Facility-Setup in a NPP)

TASK No. 1 - PHOSPHORIC ACID

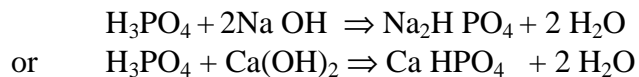
In the 1980s, 3 m³ of 60 % phosphoric acid were used for the decontamination of certain machinery, and for certain reasons were sent from Germany to the Nuclear Studies Center at Mol/Belgium for conditioning into waste products ready for a German interim store or repository. The phosphoric acid was loaded with 24 g/l iron, total activity was 50 GBq. Later it was determined, that treatment in Belgium was not possible, so the material had to be shipped back to Germany, together with other unprocessed or partially processed German waste streams sent to Mol, which after discovery in 1987 lead to a major radwaste scandal in Germany.

In 1993, GNS was entrusted to take care of all those waste streams that had to be returned to Germany and treated in order to meet the acceptance criteria of the interim stores and of the final repository.

For the phosphoric acid the technical solution was

- transfer of the acid into an aqueous salt solution or a pumpable dispersion by neutralization, and
- vacuum drying by the FAVORIT process.

Initially, laboratory tests were carried out in order to define the neutralization medium, as which either sodium hydroxide or calcium hydroxide in form of lime-milk were foreseen, leading to the following reactions:



Neutralization of the acid with 33 % sodium hydroxide lead to a temperature increase in the solution to about 90 °C, and after cooling to below 50 °C a crystal block consisting of Na₂HPO₄ plus up to twelve molecules of water as crystal water was formed. So, before volume reducing drying, the solution had to be kept at a temperature above 50 °C, or had to be diluted with water to about 8 %.

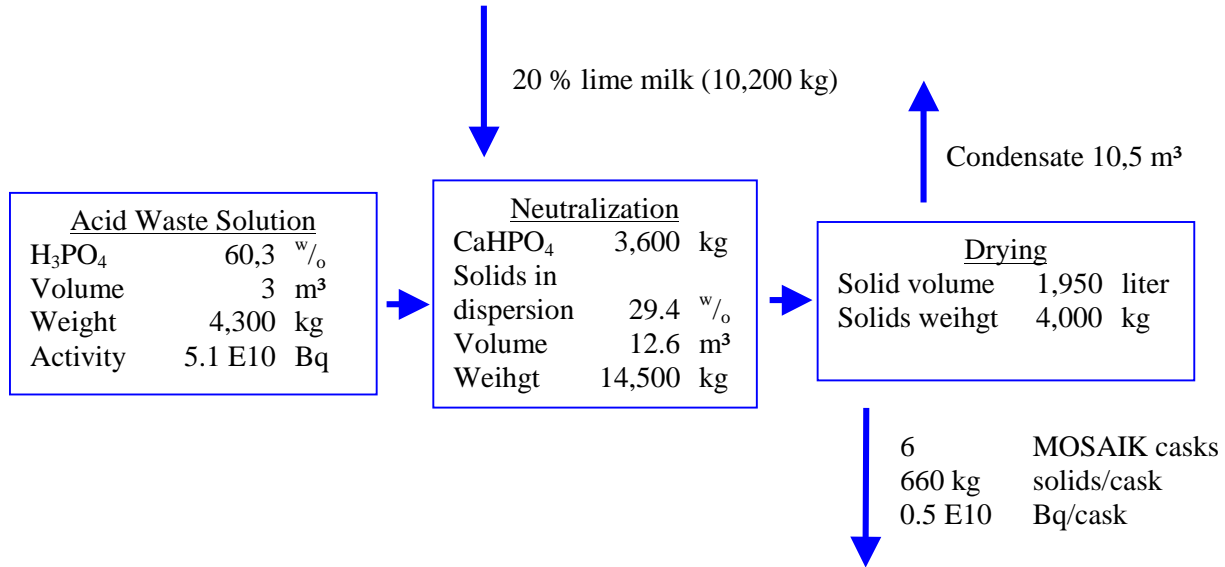
The formation of a water-free Na₂HPO₄ salt block by drying appeared to be impossible. During the drying process the solution is transferred into a melt of the salt in its own crystal water, appearing as a rather viscous substance. Further extraction of water during the drying process lead to a fluffy, highly porous mass which increased in volume as drying continued. This would have led to serious impacts on the operation of the FAVORIT facility.

On the other hand, neutralization of phosphoric acid with calcium hydroxide lead to a fine grained precipitate in water. If neutralization is carried out above 70 °C it is crystal water free.

The dispersion of CaHPO₄ in water could easily be vacuum dried, leading to a solid block with low compressive strength of chalk-like appearance. It contains small pores and is permeable for water vapor.

Neutralization of the phosphoric acid with calcium hydroxide was selected for technical application.

The stoichiometrical relations are shown in Fig. 3.



(Fig. 3: Neutralization of Phosphoric Acid with Calcium Hydroxide and Drying by FAVORIT Process - Stoichiometrical Relations)

Due to the porous nature of the precipitate and for process optimization, it was decided to co-process the phosphoric acid together with 10 m³ of evaporator concentrate from the owner of the phosphoric acid.

The entire process was to be carried out at the site of the Karlsruhe research center, where GNS's stationary FAVORIT facility is operated on rented space.

The phosphoric acid, contained in 19 200-liter-drums with internal polyethylene layer had to be shipped from Mol to Karlsruhe. Shielding was provided by insertion of the drums into 19 standard nodular cast iron casks (Type MOSAIK) which are qualified according to the transport regulations. For protection against spilling and subsequent corrosion of the cast iron casks, each drum was surrounded by a polyethylene bag.

At Karlsruhe, the phosphoric acid was transferred from the drums into a 10 m³ stainless steel tank, where the neutralization with lime milk was carried out. The emptied drums were rinsed and dried and subsequently high-pressure compacted as radioactive waste.

After neutralization the dispersion was transferred by tank truck into the entrance tank system of the FAVORIT facility.

The evaporator concentrate for co-processing was transported from the power station into the entrance tank system of the FAVORIT facility.

Drying of the material was performed without problems, leading to 15 MOSAIK casks filled with dried waste product.

The products have been shipped to the Gorleben interim store, where they are stored under safe conditions.

TASK No. 2 - OXALATE SOLUTIONS

In 1992, a decontamination campaign of the primary circuit in one NPP under decommissioning, lead to over 33 m³ of oxalate containing aqueous solutions. Total activity content was 2.2 E12 Bq, total solid content was some 2,000 kg as oxalates with some additions of citrates and EDTA.

The task was to process this liquid waste in order to meet the acceptance criteria of the interim store and the final repository.

Early tests in the laboratory confirmed that the material could be dried by the FAVORIT process resulting in a solid metal oxalate salt block.

It was known that oxalate salts dissociate at temperatures above 150 °C, leading to gas-formation, basically as CO₂ and CO.

According to the acceptance criteria of the final repository, waste packages must remain stable if subjected to a fire at 800 °C for 1 hour. If the oxalate salts were contained in standard nodular cast iron casks, under these conditions the waste product would be heated up to above 150 °C, leading to an intolerable pressure buildup in the waste package.

Consequently, attempts were undertaken to de-organize the oxalates and to transfer the oxalate solution into an inorganic solution before drying.

The standard way, which would have been to subject the solution to ultra violet light, failed due to the opaqueness of the solution.

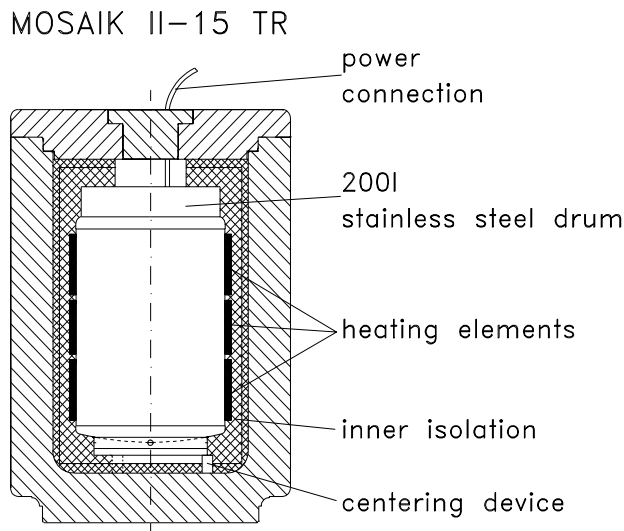
Another attempt was to oxidize the oxalates with hydrogen peroxide. Laboratory tests showed that neutral or alkaline oxalate solutions do not react with hydrogen peroxide, however a reaction in acid solution should have been possible. Subsequent laboratory tests of oxalate solutions with addition of sulfuric acid showed only a very slow reaction rate, so this method had to be disregarded.

A third possibility, namely to oxidize the oxalate with potassium permanganate had to be disregarded too, as this would have lead to considerable expenses, together with time consuming licensing efforts, for process equipment.

After the efforts to de-organize the oxalate solutions by chemical means had failed, the processing proposed by GNS was to dry the material with the FAVORIT facility, but to protect the final waste product from the heat impact by the accidental fire by a special design of the waste package. The main features were:

- a special design 200 liter stainless steel drum for drying and accommodation of the waste product,
- surrounded by a “lost” electrical jacket heater
- both surrounded by thermal insulation,
- all inserted into a nodular cast iron cask with standardized dimensions.

Fig. 4 shows the arrangement of these features in the waste package. Processing of the oxalate solutions was undertaken by a mobile FAVORIT facility in the NPP.



(Fig. 4: Cask Arrangement for Organic Salt Contents)

The treatment of a first batch of oxalate solution processed into 6 waste casks simultaneously exhibited a tolerable drying rate of initially 275 liter per day which after ten days however was reduced to one third. It had been decided to stop further treatment, after each drum was filled with about 140 kg of solids.

The reason for the reduction of the drying rate appeared to be scale formation on the inner surface of the drum, thus preventing heat transfer.

For treatment of the second batch, metal fins were attached in longitudinal direction onto the inner surface of the drum, leading towards the center of the drum, and the control of the heating had been improved. By these means the drying rate improved considerably, and treatment of this batch was completed when every drum was filled with about 190 kg of solids.

The complete amount of the oxalate solution has been processed into 12 waste packages, the properties of which are exhibited in Table 1.

Batch No.	Liquid Waste Intake	No. of Waste Packages Produced	Total Solids	Total Solids per Package	Aktivity per Package	Dose Rate	
						Surface	1 m
	m ³		kg	kg	Bq	μSv/hr	μSv/hr
1	17,2	6	820	135	1.5 E11	300	50
2	17,0	6	1,120	185	2.0 E11	300	50

(Table 1: Treatment of Oxalate Solution by the FAVORIT process. Results)

CONCLUSIONS

Both campaigns demonstrated that processing of “exotic” liquid radwaste forms are possible with the FAVORIT facility. It may however be necessary to find the right way of pre-treatment of waste, or to find the right engineering solution, should pre-treatment cause problems.