EQUIPMENT AND PROCEDURES FOR CONCRETE SOLIDIFICATION OF RADIOACTIVE WASTE FROM SYSTEMS DECONTAMINATION

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ABSTRACT

A plant for the solidification of low and intermediate level waste into concrete (FATIMA) was designed and constructed. The main objectives were versatility, simplicity and economy. The equipment thus allows operation with widely different parameters including the feed rate of the cement, the speed of rotation of the stirrer, the composition and the type of container. FATIMA was also designed to be easy to transport and to accommodate. At present, FATIMA has been used for the following tasks: a) Pretreatment of simulated waste from systems decontamination and solidification of the waste into concrete, b) Solidification of real waste from systems decontamination using Envirostone (gypsum together with an organic binder).

The simulated waste comprised several complexing agents together with ion exchange resin. The presence of such complexing agents affects the curing of the concrete. A pretreatment step where the complexing agents were decomposed through wet oxidation was therefore carried out in the waste containers. The waste was then solidified using Portland cement. The waste concrete became homogeneous and had a compressive strength exceeding 20 MPa even after immersion in water for several months.

The real waste originated from decontamination of the lower parts of a steam generator at the Kori 1 reactor (Westinghouse) in Korea. The radioactivity content of the waste was estimated to a few hundred Curies. The solidification was carried out in five liners of 50 cubic feet (1.4 cubic meters) inner volume. Envirostone was choosen as the solidification matrix due to its versatility in incorporating different chemical species and to the proven experience of it in the United States. The operation went very well and the waste was solidified within two days.

BACKGROUND

The primary purpose of the design and construction of FATIMA (Fullskale Anläggning för TestIngjutningar av Medelaktivt Avfall = full-scale plant for test solidifications of intermediate level waste) was to enable full-scale experiments and verifications of concrete solidification procedures in a versatile, simple and economic way.

In the present paper, a brief presentation will be made of the design of FATIMA together with the specifications and the operation procedures.

One type of wet waste that needs special attention in connection with concrete solidification is waste from systems decontamination. In addition to the "conventional" problem of solidifying ion exchange resin one here also has to deal with the presence of complexing agents such as ascorbic acid, citric acid, ethylene diamine tetraethyl acetic acid (EDTA) and oxalic acid. These complexing agents affect the curing of the concrete in a negative way and thus only very small amounts can be tolerated in each waste package unless some special precautions are taken. Furthermore such complexing agents may promote the migration of radionuclides in a final repository. Thus, in connection with shallow land burial in the United States, for instance, only limited amounts of such agents are tolerated.

Previous laboratory scale work at STUDSVIK[1], has indicated a possibility to avoid the above disadvantages. The complexing agents were shown to decompose relatively rapidly under certain pH, oxidation and temperature (< 100 °C) conditions. It was also shown that the wet oxidation was relatively selective in the sense that the complexing agents were decomposed relatively easily compared to the mixed bed ion exchange resin. The previous work also included test solidifications where the concrete was able to accommodate more reasonable amounts of waste without any problems with the curing, and with good product properties.

In the present paper, a full-scale verification of the procedure will be presented together with some supporting and supplementary laboratory investigations. This part of the work was carried out at STUDSVIK on contract by SKB (The Swedish Nuclear Fuel & Waste Management Co). The composition, container, operation procedure etc. used resemble those used at the Oskarshamn and Ringhals power plants in Sweden. Some of the general background on waste solidification in Sweden may be found in Refs. 2-5.

During the summer 1984, Pacific Nuclear Systems Inc. (PNSI) in collaboration with the Korea Atomic Services Company (KASCO) carried out a system decontamination on one of the steam generators of Kori 1 (which is a PWR of Westinghouse design). The commission also included solidification of the waste into Envirostone using FATIMA, which was supplied by STUDSVIK. The stirrers and containers as well as the shielding used were supplied by PNSI/KASCO.

Envirostone was supplied by the US Gypsum Company. It contains gypsum together with an organic binder and is well-known for its ability to solidify wet waste containing widely different chemical species into stable waste forms [6].

The solidification of the waste will be briefly described in the present paper.

THE SOLIDIFICATION EQUIPMENT

A drawing of the solidification plant is shown in Fig. 1. The main parts are the following:

- Main structure including legs, crossbars and the stair-case.
- Trolley for moving the container/waste form in and out, including rails (not shown in Fig. 1).
- Radiation shielding for the waste container (not shown in Fig. 1).
- Silo for cement.
- Screw feeder for cement.
- Motor and gear-box for stirrer.
- Feed unit including cover that docks onto the container and a flange attachment to the gear-box of the motor.
- Crane (for motor, gear-box and feed unit).
- Electrical installations.

The legs of the main structure are extendable. In the contracted position, only the feet and a short piece of supporting beam remain below the upper level. This feature enables the height of the plant to be reduced which facilitates transportation so that e.g. an ordinary lorry can be used.

All electrical equipment is connected to a few casings located together on the superstructure. All controls and indicators are collected in a central control box which is connected to one of the casings through a long cable.

The procedure for operation of the equipment is typically as follows: Waste is fed into the waste container and the container is put in its position. (The waste can also be entered after the container is put in its position.) The crane is lowered and the feed unit is docked onto the upper part of the container and/or shielding. At the same time, the torque transfer from the gear-box to the dispensable stirrer is secured as well as the pipes for ventilation, addition of cement, additives etc.

The main motor is started, certain chemicals added, and the cement feed is turned on. The process is closely followed up by control of the cement feed, the power consumption of the motor of the stirrer and by control of the angular speed of the stirrer. The mixing is terminated when certain conditions are fulfilled.

Finally, the feed unit is raised and the waste container removed.

The feed rate of the cement can presently be varied between a few and a few hundred kilograms per minute, and a large part of this variation can be carried out during operation. The speed of the main motor can be varied continuously between zero and about one rps, while the stirrer is turned on. The maximum torque obtained using the motor and gear-box installed is close to 1 KNm, which is sufficient for batches of waste-cement mixtures up to several cubic meters. The capacity of a plant of this type depends primarily on the process, stirrer and container chosen. For instance, the processing of one cubic meter of the simulated waste-cement mixture discussed below required less than two hours, and the solidification of about 7 cubic meters of real waste-cement mixture also discussed below required two days.

PRETREATMENT AND SOLIDIFICATION OF SIMULATED WASTE

The full-scale pretreatment and solidification of simulated waste from systems decontamination was preceeded by several laboratory tests. As described in the introduction, some of these dealt with the influence of pH, oxidation and temperature conditions on the decomposition of the waste and on the properties of the solidification product. Other experiments dealt with temperature rise problems, formation of carbon monoxide and adjustment of the consistency of the concrete.

The type of ion exchange bead resin used had a dry weight content of about 40 % when unloaded and in the undrained form. The resin used in all the tests had 16 % loading (calculated on dry weights) of decontamination agents such as citric acid, ascorbic acid, ethylene diamine tetra ethyl acetic acid (EDTA) and oxalic acid. Laboratory scale tests on somewhat diluted samples indicated that, in the full-scale, the temperature would become tens of degrees above 100 ^{o}C if boiling were prevented. Thus, in order to avoid boiling in the full-scale, some special provisions had to be made in order to improve the cooling and thus obtain reasonably short processing times.

Furthermore, some of the decomposition reactions are known to produce carbon monoxide. Any such gas must be carefully vented away since its maximum permissible exposure limit in the air at a plant is only 35 ppm in Sweden at present. The conditions for carbon monoxide formation were therefore studied in the laboratory scale. The result was, not surprisingly, that the largest amounts are formed in the beginning of the process when the solution is comparatively strongly reducing. The maximum content of carbon monoxide in the gas released was 1.3 % by volume.

The venting as well as the cooling needed in the full-scale were achieved by connecting the upper part of the waste container to a reflux condenser which, in turn, was connected to the air exhaust system. With this supplement to FATIMA, water vapor from the warm waste mixture was dissolved in the air and condensed in the reflux condenser from which it poured back into the waste container.

Other laboratory scale experiments dealt with the characteristics of different mixtures of simulated pretreated waste, water and cement. It was checked that the different relevant properties of the waste were acceptable. The composition selected had a consistency and a curing time similar to those of the standard processes used in Sweden. Thus, the homogeneity of the simulated full-scale waste form is expected to be as good as that of the waste from the

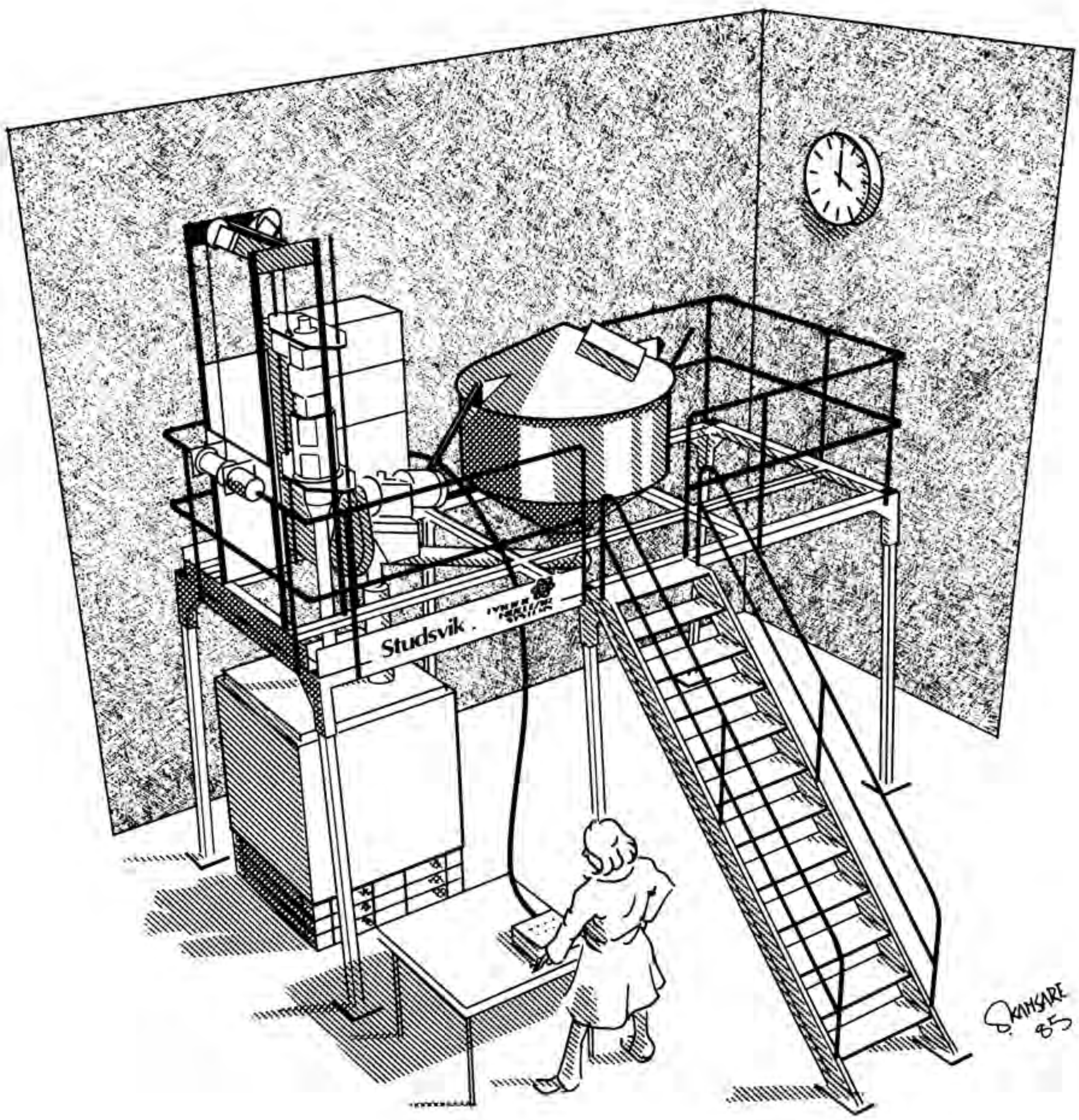

Fig. 1. A drawing of the equipment used for the full-scale solidifications of simulated and real waste into concrete, FATIMA. The different parts of the equipment are described in the text. (The floor of the superstructure has been removed for clarity.)

standard process. The selection of the composition was conservative and the waste loading (based on dry weights of ion exchange resins and complexing agents) was about 90 % of those used in the standard recipies Acceptable product properties can probably be obtained for substantially higher waste loadings, however.

The full-scale pretreatment was carried out in the following way. Mixed bed bead ion exchange resin was loaded with the complexing agents in water solution and the mixture was charged to the waste container. The waste container had an inner volume of about one cubic meter. The walls were 10 cm thick and were made of reenforced concrete. The dispensable stirrer was turned on together with the ventilation and the reflux condenser. Some acid was added whereafter the oxidizing agent was added in batches of about 3 % of the total every five minutes. The temperature rose rather promptly after each addition as can be seen in Fig. 2. The addition of oxidizing agent was interrupted when the temperature reached 85 °C and resumed when it had decreased to 70 °C. An insignificant amount of foam was observed after the initial addition of oxidizing agent; it dissappeared within a couple of minutes.

The pretreatment went very smoothly and no dificulties were encountered.

The solidification was carried out after a couple of days when the waste had cooled to room temperature.

A pH adjustment was made with the stirrer on high speed whereafter certain chemicals were added in order to improve leach properties, water resistance, and frost resistance of the waste product together with the consistency of the uncured concrete.

The stirrer was kept on high speed while the cement was added. The feed and mixing times were about the same as in the standard process - sufficiently long to enable a good mixing and sufficiently short to be completed before any substantial increases in consistency due to the curing of the concrete appeared. The mixing was inspected regularly during the processing, and records were made of the speed of rotation of the stirrer as well as of the power consumption, which also were similar to the ones encountered for the standard processes used in Sweden.

The solidification went very smoothly and no difficulties were experienced.

When the solidification was completed, samples were taken for analyses of different kinds. For instance, the compressive strength after one month of curing in air was determined to 26 MPa. Another sample was cured in air for one month and immersed in water for another month. A visual inspection indicated a good water durability and the compressive strength was determined to 28 MPa.

SOLIDIFICATION OF WASTE FROM STEAM GENERATOR DECONTAMINATION

FATIMA was transported (by air cargo) to the waste treatment plant at the Kori 1 reactor near Pusan in South Korea. The waste had been put in five 1.4 cubic meter liners. The liners were made of mild steel and were cylindrical in shape. They were all provided with dispensable stirrers. The waste liners fitted into either of two radiation shields. They were made of outer and inner containers of mild steel plate with about 20 cm of concrete in between. The liners were initially filled to two thirds of their volume with waste. The waste comprised sludge and other components extracted from the steam generator, decontamination chemicals including complexing agents and bead ion exchange resin. One liner contained cationic resin and the others a mixture of an-ionic and cat-ionic resin.

The solidification agent to be used was Envirostone[6]. It consists of gypsum together with an organic binder. It is readily dispersed in water and the mixture has a comparatively low viscosity. It can incorporate a great variety of wet wastes, at least after some additions of agents that adjust the pH, retard the curing or emulsify hydrophobic species. Laboratory tests carried out by the manufacturers and others include corrosion resistance, container integrity, thermal stability, compressive strength, combustibility, water durability, leach properties, etc., and the solidification agent meets US DOT and NRC specifications and regulations including NRC 10CFR61.

Several inactive laboratory scale and full-scale tests were carried out at the Kori site prior to the hot solidification in order to verify suitable compositions and amounts of retarders to be used and to test the solidification system.

Typically the hot solidifications went as follows: FATIMA, supplied with castors, was rolled over a shielded liner, positioned and docked onto the liner by lowering of the feed unit. The stirrer was turned on and a small amount of Envirostone was added together with the retarder. Then, about 800 kg of Envirostone was added during less than half an hour. The stirrer was kept on for some additional time to ensure a good homogeneity. The curing then took place within a few hours from the termination of the mixing The curing process was monitored by penetration tests together with visual inspections. After curing, an inactive Envirostone/water mixture was poured on top in order to cap the liners.

The total radionuclide content of the liners was estimated to a few TBq. The surface dose rate of the shielding of the liners was about 0.2 mSv/h and this value was reduced to about 0.1 mSv/h after solidification. The total exposure to the personnel was estimated to be less than a few mmanSv.

The solidification of the five liners was completed in two days. The over-all experience was that both the equipment and the solidification procedure worked very well.

DISCUSSION AND CONCLUSIONS

Concrete solidification of waste from systems decontamination requires special attention for several reasons:

- The content of complexing agents may require special arrangements for the final disposal (e.g. shallow land burial in the US).
- The presence of complexing agents may imply that the charge/cost for final disposal becomes considerably higher.

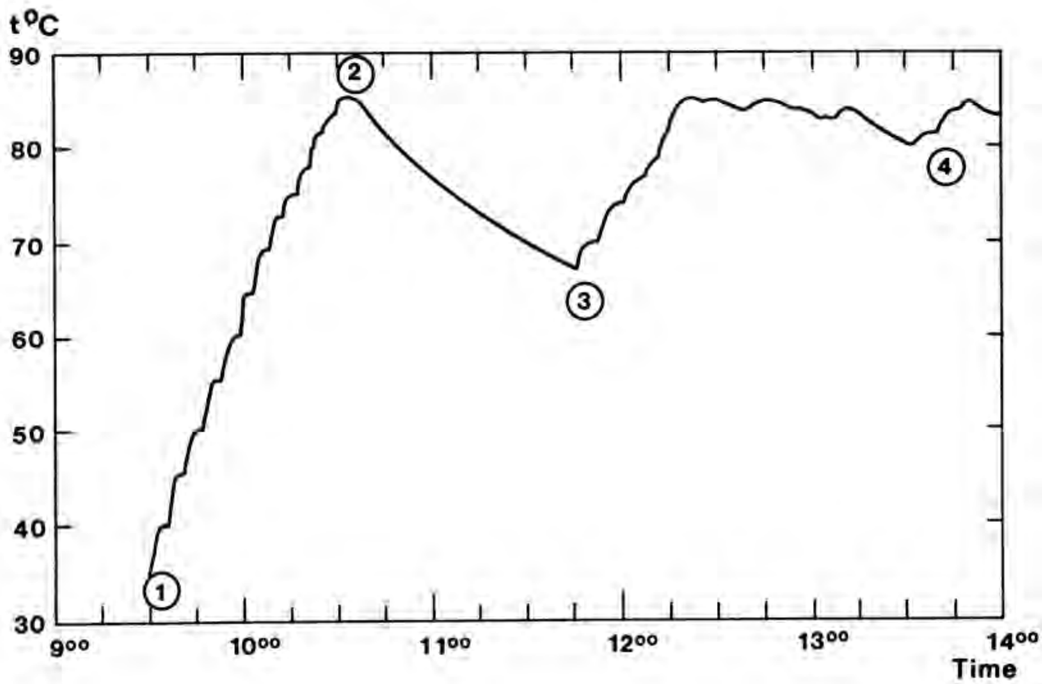

Fig. 2. Temperature versus time for the full-scale pretreatment of simulated waste from systems decontamination. The addition of oxidizing agent was started at /1/ and interrupted at /2/. After a cooling period between /2/ and /3/, the addition was resumed at /3/ and terminated at /4/.

- The rate of curing as well as the inhibition time are frequently strongly affected by the presence of typical decontamination chemicals.
- The consistency and thereby also the homogeneity may also be altered considerably by the presence of decontamination chemicals.
- The composition of waste from systems decontamination may vary considerably due to:
  - o different types of chemistries
  - o different materials and systems to decontaminate
  - o different species are absorbed on different filters etc.
- The composition of the waste may affect the characteristics of the waste form e.g.
  - o water durability
  - o compressive strength
  - o leach rate
  - o radiation stability
  - o biological stability

These topics all need attention if acceptable product properties and good economy are to be achieved.

It has been illustrated above that the equipment needed both for full-scale tests and for treatment of at least moderate amounts of real waste can be rather simple (and thereby also inexpensive). FATIMA can perform the same operations on the waste as many larger and more complicated plants. Due to the simple design it also offers a large flexibility with regard to stirrer, container and shielding design, as well as operation parameters. This flexibility is illustrated above by the utilization of it in two widely different processes. The transportation features described above add to the flexibility not least in connection with solidification of occasionally appearing waste from systems decontamination. Finally, FATIMA requires rather little from the premises (water, ventilation, electric power, space etc.). For instance, its dimensions in the operating position are approximately 4.9 m (height), 4.9 m (length) and 2.4 m (width). FATIMA could thus, if desired, be fitted into a space inside the containment of a PWR.

It is imperative that laboratory scale and full-scale tests are performed prior to the solidification of waste from systems decontamination. This is certainly the case for Portland cement but also for Envirostone, where the curing time (and the amount of retarder needed) was experienced to be rather strongly dependent on the composition of the waste.

For the Portland cement solidification, it is demonstrated above that:

- The amount of complexing agents can be reduced to small quantities by using the pretreatment procedure.
- The pretreatment procedure can be carried out in an ordinary solidification plant with only minor supplements to the equipment.
- The amount of waste in each container is about the same as for other waste streams comprising mainly ion exchange bead resins.
- The properties of the waste, including the homogeneity, are comparable to those obtained in ordinary solidifications.

For the Envirostone solidification it has been demonstrated that:

- Real waste from a system decontamination can readily be solidified into Envirostone.
- The variations in the waste implied only limited and acceptable variations in the composition, process and curing time.
- The process controls together with the background work[6] ensures the properties of the products.
- The waste stream packaging efficiency is comparable to other, regular, solidifications into Envirostone[6].

It is probably too early to make conclusions as to which of the two processes is the preferable one. Envirostone was chosen for the hot solidifications for its versatility in incorporating different chemical species and for the proven experience of it in the US. It was also chosen in view of the short time available for the solidifications which did not allow the time needed for adjustments of the process utilizing destruction of the chelating agents.

It appears at this point that Envirostone may enable a somewhat higher waste stream packaging efficiency while Portland cement would offer a lower price of the solidification agent. Furthermore, the cost at the disposal site (e.g. for shallow land burial in the US) may be significantly reduced if the complexing agents have been destroyed.

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