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PILOT PLANT EXPERIENCE ON HIGH-LEVEL WASTE SOLIDIFICATION AND DESIGN OF THE ENGINEERING PROTOTYPE VERA

by

W. Guber, W. Diefenbacher, W. Hild,
H. Krause, E. Schneider, G. Schubert

Gesellschaft für Kernforschung Karlsruhe

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Kurzfassung

In der vorliegenden Arbeit wird das im Kernforschungszentrum Karlsruhe entwickelte Verfestigungsverfahren für hochaktive Abfallösungen vorgestellt. Es besteht im wesentlichen aus den Schritten Denitrierung, Kalzinierung in einem mit überhitzten Dampf beheizten Sprühkalzinator und Schmelzen des Kalzinats mit den entsprechenden Zusätzen in einem Induktions-Schmelzofen zu Borosilikatglas. Über die bisherigen Betriebserfahrungen mit der inaktiven 1 : 1 Pilot-Anlage wird berichtet. Des weiteren wird eine Beschreibung der geplanten Mehrzweck-Versuchsanlage VERA 2 gegeben, die für die Aufarbeitung der hochaktiven Abfallösungen aus der ersten deutschen Wiederaufbereitungsanlage WAK vorgesehen ist.

Abstract

In the present paper the solidifaction process for highly active waste solutions as developed in the Karlsruhe Nuclear Research Center is presented. Its principal steps are: denitration, calcination in a spray calciner operated with superheated steam, melting of the calcine with appropriate additives to borosilicate glass in an induction-heated melting furnace. The operational experiences gained so far in the inactive 1 : 1 pilot plant are reported. Furthermore, a description is given of the projected multi-purpose experimental facility VERA 2 which is provided for processing the highly active waste solutions from the first German reprocessing plant WAK.

1. INTRODUCTION

At present, solidification facilities for high-level waste (1WW) solutions containing fission products are not yet regarded as an absolutely necessary part for the operation of reprocessing plants. However, the solidification of those wastes - which so far have been stored as liquids everywhere - would contribute greatly to the safety of reprocessing plants. Converting waste solutions into solid products suitable for ultimate storage can reduce the inventory of fission products in these plants as it allows disposal of wastes to be carried out practically together with their generation.

For the moment, only the 4o t/yr prototype reprocessing plant for spent nuclear fuels (WAK) is in operation in the Federal Republic of Germany. The small amounts of 1WW arising there are stored for the time being as nitric acid solutions in stainless steel tanks. Due to safety considerations in relation with the geologic, hydrologic and meteorologic conditions and the high population density the objective of the German policy was from the very beginning to store the fission product solutions only for a limited period of time as a liquid and to convert them as early as reasonable into inert, chemically stable, irradiation- and temperature-resistant solids, thus reducing the risk of release and dispersion of radioactivity. These solid products (e.g. glasses or ceramic materials) should finally be disposed of in rock salt formations and in this way safely isolated from the biocycle for the long periods of time necessary for decay of nuclides to activity levels which do no longer raise any hazard to man and his environment.

An appropriate solution of the high-level waste problem becomes still more important with regard to the anticipated 1,500 t/yr reprocessing plant which will start active operation during the early eighties.

Since several years, the Nuclear Research Center at Karlsruhe performs an extensive R + D program in the field of high level waste management. The first lab-scale activities were devoted to the definition of appropriate solids for fission product solidification and have resulted in the selection of borosilicate glasses for starting industrial solidification of 1WW from WAK. In addition to this work which is described together with other investigations on advanced solidification procedures in another paper read at this conference [1], technological development work has been executed.

The results of the lab-scale R + D work and a thorough literature study on high-level waste solidification processes under investigation elsewhere have confirmed the initial assumption that a continuous procedure allowing scale-up to higher throughputs meets best the requirements of the German situation. Consequently, the technological R + D work was devoted to the following objectives:

- conception, design, construction and operation of an inactive pilot unit on 1 : 1 scale;

- planning and realisation of a multi-purpose experimental facility for solidification of high-level fission product solutions (Project VERA).

Initially, the VERA plant was planned to be built in direct vicinity of the inactive pilot unit; another industrial plant for routine solidification of 1WW was projected on the WAK site. Detailed studies lead to the decision that both the industrial and R + D interests could be combined into a single plant located near the 1WW storage tanks on the WAK site. Designing work for this plant (VERA 2) started in late 1971.

2. GENERAL DESCRIPTION OF THE SOLIDIFICATION PROCESS

None of the experimental vitrification units built in other countries has proved to be the optimum for the conditions at Karlsruhe. Therefore, it was attempted to adopt those process steps and components of foreign installations which are best suited to the situation prevailing here and to combine them with special developments to an optimum process which operates continuously and can easily be adapted to large throughputs by scaling up.

The fundamental steps of the process selected are as follows:

- denitration of free nitric acid and heavy metal nitrates of 1WW by reaction with formic acid;

- drying and calcining in a spray calciner;

- incorporation of the calcine into glass by melting with suitable components and casting the melt into final storage containers;

- off-gas purification.

2.1 Denitration

A denitration procedure has been developed to destroy the free nitric acid and as much fission product nitrates as possible in the 1WW, with the aim of avoiding oxidizing conditions during calcination and glass melting (i.e. ruthenium-volatilisation) and producing an off-gas that can be purified without complication. The overall chemical reaction can be described by the following formula:

$$2\ HNO_3 + 4\ HCOOH \rightarrow N_2O + 4\ CO_2 + 5\ H_2O; \quad \Delta H = -2o2\ Kcal.$$

Both discontinuous and continuous operation modes at boiling temperature are possible. The following average off-gas composition has been found in discontinuous operation by introducing simulated 1WW (4 M HNO_3) into the appropriate amount of concentrated formic acid:

CO_2	:	78 vol.o/o
N_2O	:	16 vol.o/o
NO	:	5 vol.o/o
N_2	:	1 vol.o/o

The main part of the NO is produced toward the end of the reaction [2]. Ruthenium losses can be reduced to values less than o,o1 o/o of the total Ru present by application of this denitration process. Heavy metal nitrates are denitrated completely [1, 3].

2.2 Drying and Calcining by Spraying

In the next process step the denitrated 1WW solution is dried and calcined by application of high temperature. The facility for this purpose was developed from a calciner similar to conventional spray driers. It is characterized by direct heating with superheated steam which is recycled. This feature presents a new and fundamental difference compared to both conventional spray driers and a wall heated spray calciner similar to that used in WSEP [4]. It offers the following main advantages:

- a minimum of non-condensable gases has to be treated as the heating medium entering the tower is condensable by itself;

- scale formation on the walls is avoided due to the particular flow pattern in the calciner and the fact that the wall temperatures are by far lower than in wall heated calciners.

Steam temperatures of 300° C are sufficient for drying. However, to achieve a satisfactory calcination, a product temperature of 450° C is needed in the tower. This can be accomplished by increasing the entrance temperature of the superheated steam to 650° C.

Efficient solid separation is of fundamental importance for the process. Therefore particular emphasis had to be put on the construction of the filter unit.

2.3 Glass-Melting and Casting

In this process step the mixture of calcine and glass components is melted to a glass and afterwards cast into the final storage container. At a temperature of about 1.200° C, the borosilicate glass selected forms a homogeneous glass melt of appropriate viscosity. Medium frequenzy heating (2,000 c/s) is used for the crucible and the storage container. This heating system offers the advantages of simple design and control as well as high reliability and allows replacement of the crucible with standard remote techniques.

2.4 Off-Gas Purification

Due to the pretreatment of the 1WW solution in the denitrator both the loss of ruthenium and the formation of higher nitric oxides during calcination and melting is drastically reduced. Thus, the further purification of the off-gas is expected not to be a major problem. No special equipment for ruthenium retention is provided.

3. INACTIVE PILOT PLANT

3.1 Description

In order to demonstrate the technical feasibility of this process, to study the optimum equipment design for the multi-purpose prototype VERA 2, and to gain operation experience, a full-scale inactive testing facility has been installed at the Decontamination Department (ADB) of the Nuclear Research Center at Karlsruhe. As shown in the block diagram of **Fig. 1**, this facility combines the essential parts of the process, i.e.,spray calcination, melting-casting and off-gas treatment, and is operated with inactive simulated 1WW solution at a rate of 1o to 25 litres/h, i.e.,at conditions meeting both R + D and WAK requirements. In addition, a denitration unit of 5o l useful volume is available that allows testing of this process in discontinuous and continuous operation in order to establish design criteria for a full-scale unit. Fig. 2 shows the general view of the plant.

The flowsheet of the spray calciner is shown in Fig. 3. The unit comprises a feed tank (1), a tower (3) (diameter: 6o cm, height: 2oo cm) with spray nozzle, a filter (8), a condenser (9), a condensate vessel (1o), a steam jet (6) and electrical heaters for the steam currents (4, 5, 7). The calciner is operated slightly under atmospheric pressure. The superheated circuit steam enters the tower at the top at 65o° C, passing a perforated plate. Steam circulation is maintained by a steam jet operating with superheated steam of 45o° C and a pressure of about 4 atm; steam of the same conditions is used for blowing back the filter candles. The two-component spray nozzle is operated by superheated steam of ≥ 35o° C at 3 atm. Under these conditions, the calcine reaches an average tempe-

FIG. 1 PRINCIPAL FLOW SHEET OF PILOT PLANT

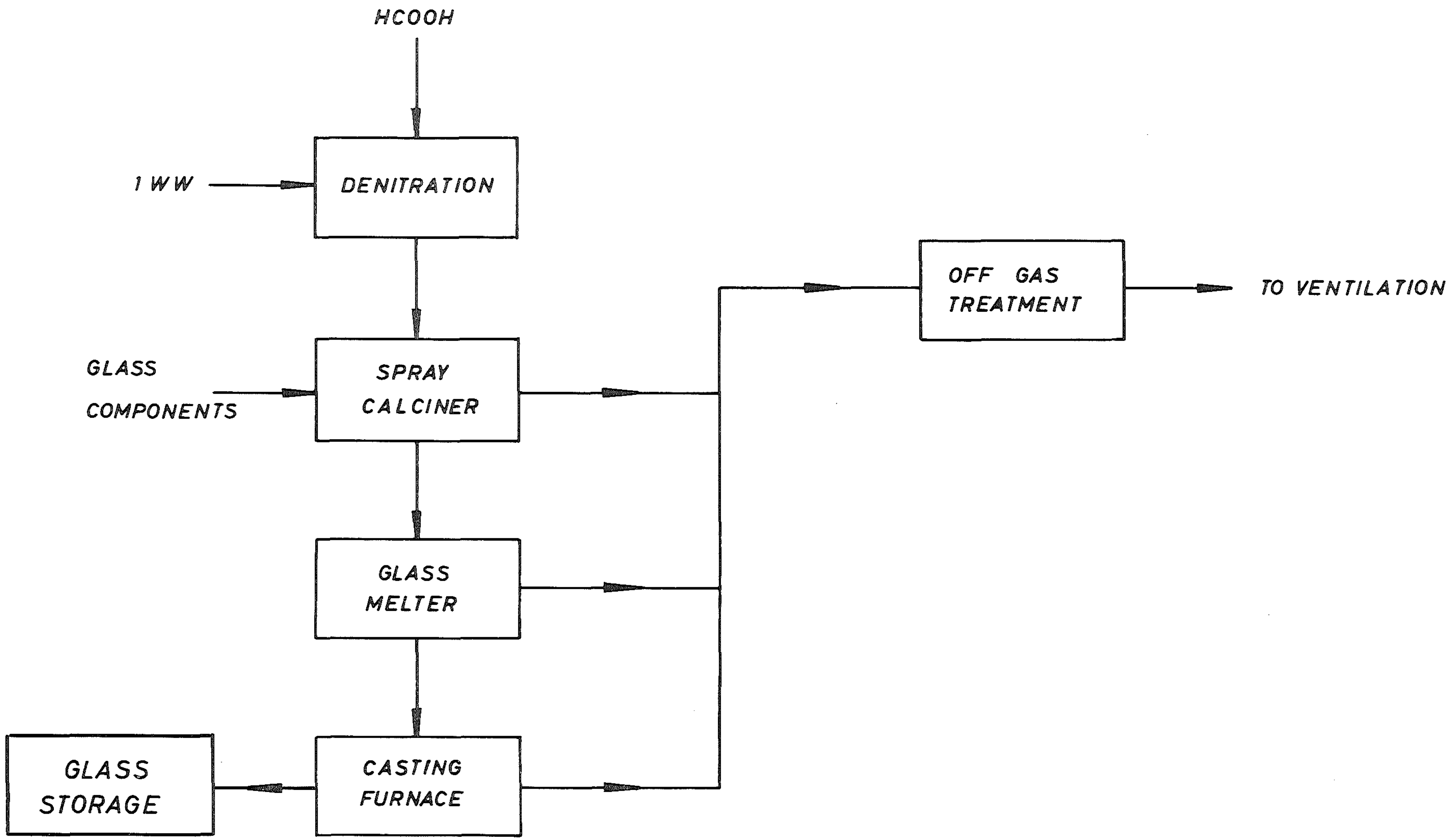
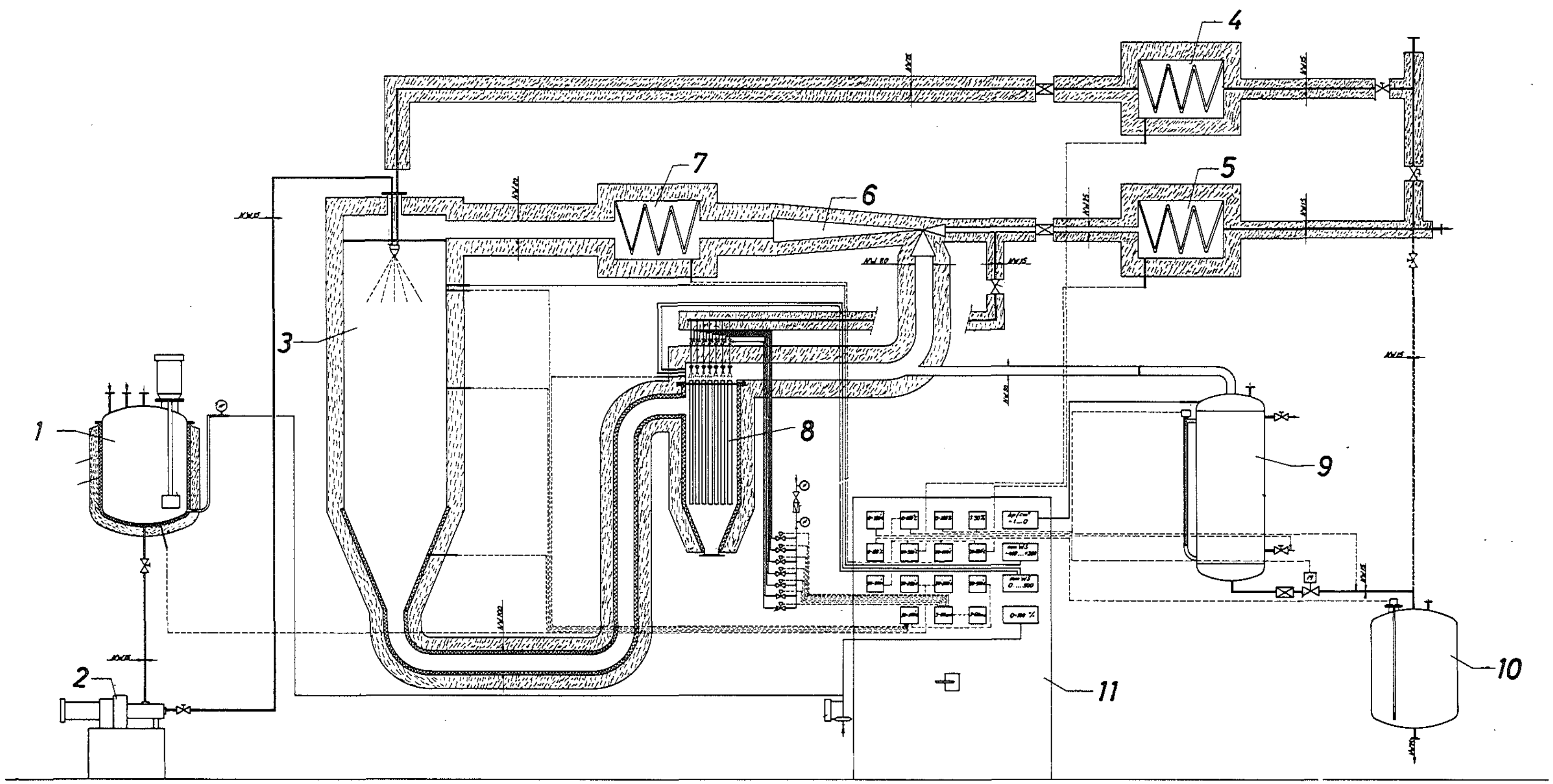


Fig. 2 General view of the inactive pilot-scale facility for vitrification of fission product solutions

1. feed tank
2. spray calciner
3. filter candles
4. vitrification furnace
5. annealing furnace
6. glass vessel removed
7. MF-induction heating unit

FIG. 3 FLOW SHEET OF THE SPRAY CALCINER



1 FEED TANK
2 FEED PUMP
3 SPRAY CALCINER
4 SPRAY STEAM OVERHEATER
5 PROPELLENT STEAM OVERHEATER
6 STEAM JET
7 CIRULATING STEAM OVERHEATER
8 SEPARATOR (CYCLON + FILTER CANDLES)
9 CONDENSOR
10 CONDENSATE TANK
11 CONTROLBOARD

rature of 450° C in the tower. It is then transported through the connection pipe to the filter by steam at a velocity of about 20 m/sec. The filter consists of sintered metal filter candles with a total surface of about 1 m^2. The crucible is mounted at the bottom of the filter housing (not shown on the flowsheet).

3.2 Experiences

The first runs of this facility took place in autumn 1970. Since that time a lot of test runs lasting from several hours to two weeks have been carried out. As usual, many difficulties have turned up. Some of them are solved today, others need further studies, especially with regard to later operation under hot conditions.

The feasibility of drying and calcining in a spray tower heated with recycled superheated steam was successfully demonstrated during the first runs. Simultaneously the basic design values of this facility proved to be correct.

In the following sections, the experiences gained with the different components of the test facility are discussed.

3.2.1 Denitration Unit

After completion of the fundamental investigations into the process chemistry [2], first tests with the small denitration unit have successfully been performed using batches of simulated 1WW solutions of different nitric acid concentration. These tests have already shown the feasibility of this particular process step; denitration can safely be carried out to any preselected value within a period of 1 to 5 hours, depending on initial nitric acid concentration and feeding conditions. Process surveillance is possible by controlling the off-gas, the redox potential and the reflux.

Tests are being continued and will be completed in a 1 : 1 unit.

3.2.2 Feed System

The contents of the feed tank must be agitated because the solid content in the feed solution increases considerably after the denitration. Effective agitation ensuring homogeneous mixing is still more important if glass components are added to the feed solution. Due to these problems, however, it is intended to add the solid glass components directly to the tower or the melter. Therefore an agitation system using a pulsing device without moving parts has been procured and is now being adapted to hot cell requirements.

In inactive operation with simulated 1WW solutions, even with those containing glass components (SiO_2, B_2O_3, TiO_2, Al_2O_3 Na_2O, CaO), the feeding problem is solved by positive displacement pumps (Mohno-, or Orlita-type). To cope with the special feeding problems in highly active operation, several pumping and metering devices are presently being tested.

3.2.3 Steam Heaters

Only the heater for the circulating steam asks for particular attention. The other heaters will not be in contact with contaminated steam and are thus considered conventional equipment.

Several heater designs have been tested, all using electrical resistance heating. A version with easily replacable heating needles has given the best results. The actually installed heater for the circulating steam has an electrical input of 45 kW and can be operated at a steam temperature of 650° C without problems. Each heating needle has a maximum power of 3.7 kW. The canning material of the heating elements is Incoloy 800. To avoid overheating of the needles, the heaters have to be equipped with temperature limit switches.

3.2.4 Spray Nozzle

As expected, the spray nozzle has required extensive development regarding both its design and its installation at the top of the spray tower.

As superheated steam is used for spraying and as the nozzle is heated from the tower atmosphere below, careful provisions have to be taken to avoid evaporation of the feed stream already inside the nozzle. This have been achieved by

- minimizing the surface of the nozzle which is in contact with the tower atmosphere ;
- cooling the feed line almost up till the nozzle outlet ;
- minimizing the heat transfer by conduction from the spraying steam line to the feed line by avoiding any direct

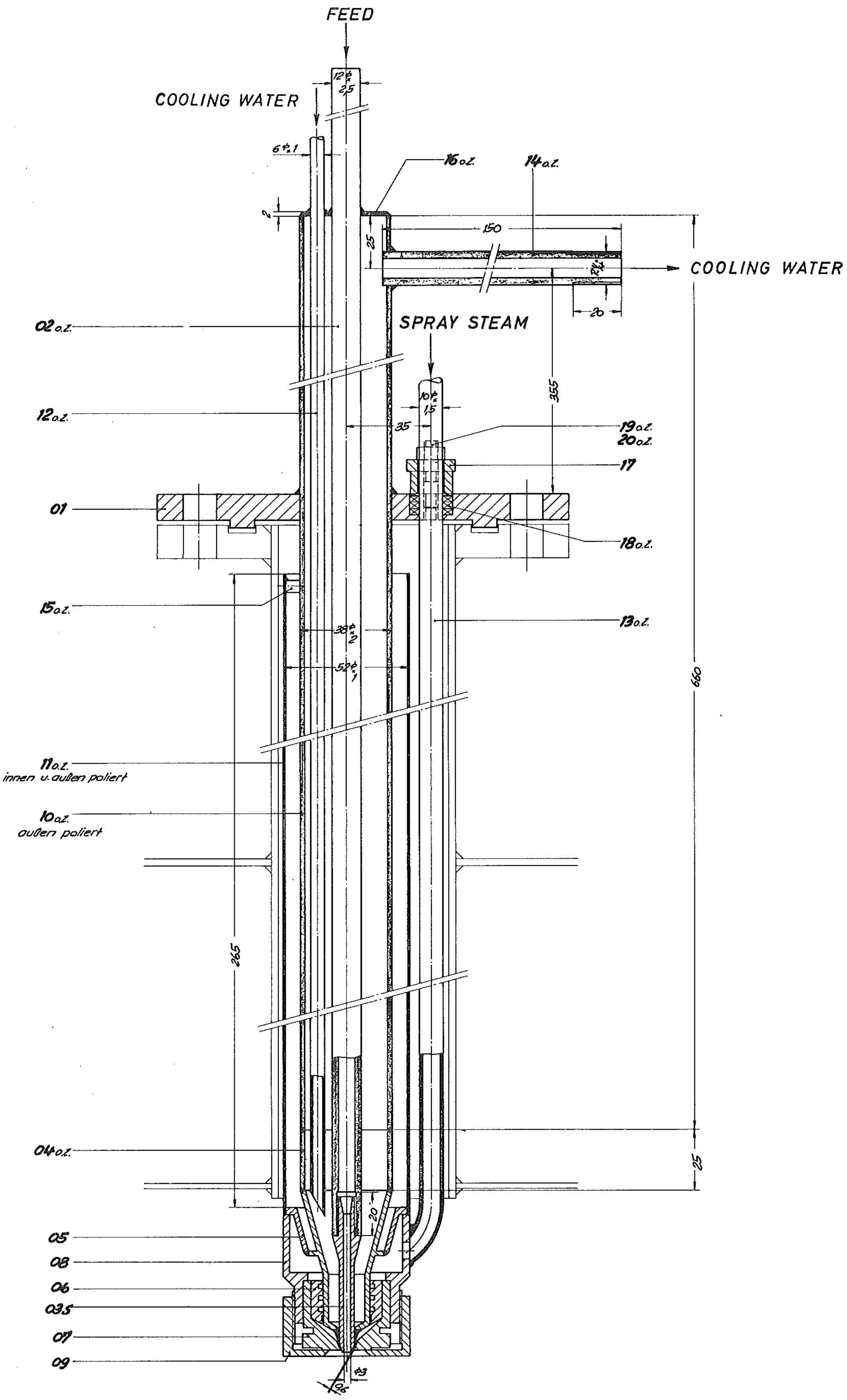


FIG. 4 SPRAY NOZZLE

contact of these lines prior to the mixing zone of the nozzle.

The design meeting these requirements is shown in Fig. 4. This particular arrangement has shown satisfactory performance in numerous test runs at feed rates from 6 to 3o litres/h with simulated 1WW solutions with and without glass components. Spraying steam of 35o^{o} C and 3 atm was utilized at a steam-to-feed ratio from o.7 to 1.o.

The nozzle design is now being adapted to the special conditions of highly active operation, i.e.,remote cleaning and replacement.

3.2.5 Calciner-Tower

The tower dimensions of o.6 m diameter and 2 m height were found to be adequate design values for the intended throughput and calcining efficiency. The temperature distribution in the tower is rather uniform without pronounced temperature gradients. The wall temperature is roughly 2o^{o} C lower than that in the tower center. A temperature decrease along the tower axis indicates that drying of the droplets is completed within roughly 6o cm below the spray nozzle. Beyond this point, the temperature is nearly constant ($\approx$ 45o^{o} C) down to the tower outlet. Under normal operation conditions an equilibrium powder deposition of less than 1 mm has been observed on the calciner walls. This powder deposit is easily removable. Scale formation has never been observed. However, it is rather important to avoid condensation inside the tower. For this reason heating and cooling of the system (start-up, shut-down) is done by means of hot air. The tower material (Inconel 6oo) has shown no corrosion as yet (1,5oo hours of operation).

When operated at the conditions described, the calcine has a water content of less than 2.5 o/o and as much as 7o o/o of the nitrates present in an untreated 1WW solution are decomposed.

3.2.6 Filter Unit

This component has required extensive development. The filter now in use consists of seven sintered metal candles (German Steel No. 1.44o1, similar to AISI 316) with a pore size of 35 µm and a total filter area of 1 m^2. Independent cleaning is possible by a special back-blowing system (Laval nozzle with diffusor).

The filter principle itself has proved to meet best the requirements. However, pressure drop measurements have indicated that the installed filter area was to small. The initial pressure drop of 1oo mm water column for the clean filters increased to as much as 1,ooo mm for the filters loaded with dust. At this pressure drop, the installed steam jet was no longer able to maintain sufficient steam circulation. The problem can be solved by increasing the filter area by a factor of 5 to 7.

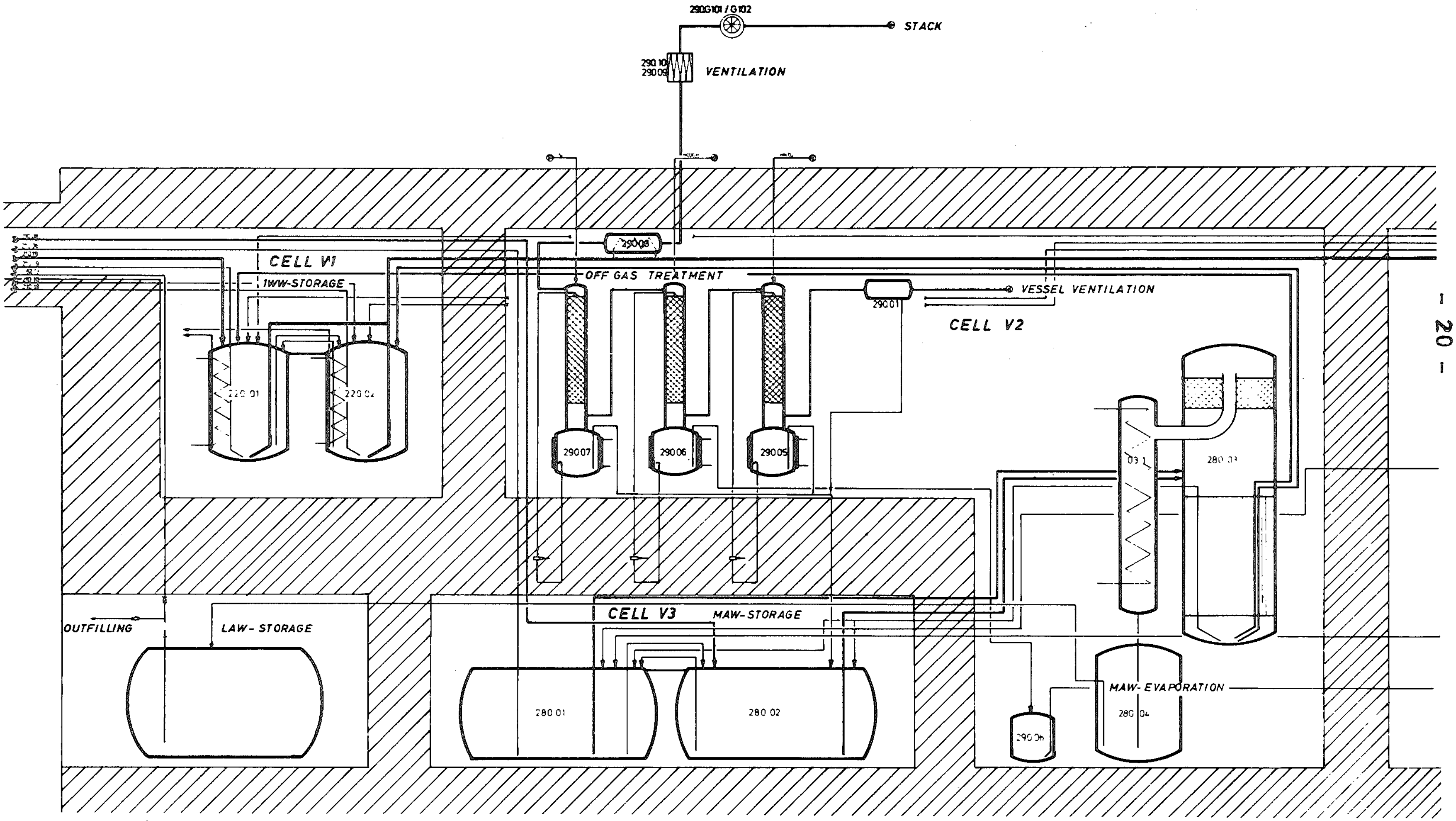
3.2.7 Melting Unit

The melting of the borosilicate glass in the Inconel 6oo crucible has not presented any major problems. The melting temperature of about 1,1oo$^\circ$ C is reached within two hours. Control of operation conditions is easily achieved. The batchwise discharge of the melt from the crucible can be started and terminated or interrupted within a few minutes by heating or cooling the discharge tube.

Continuous discharge of the melt by an overflow has not been realized, due to the difficulties encountered with small flow rates.

During the first test runs, the calcine/glass component mixture tended to plug the crucible inlet, because the temperature in this region exceeded the softening point of the mixture. This could be avoided by lowering the surface temperature of the critical parts by changing the geometry of the crucible and providing additional cooling.

FIG.5 FLOW SHEET I OF THE VETRIFICATION UNIT VERA 2



4. ENGINEERING PROTOTYPE VERA 2

The project VERA 2 comprises a hot-cell facility for the solidification of high-level wastes. The aims of this installation are

a) demonstration of the solidification process described above with original high-active waste solutions;

b) routine solidification of the 1WW-solutions from WAK;

c) development and testing of advanced methods for solidification and of new products.

The glass blocks produced will be used for performing storage tests at the Asse salt mine and for demonstrating safe storage techniques.

To preserve the multi-purpose character of VERA 2 it is intended to mount as far as possible flexible installations and to use for the main units the so-called rack techniques for easy change and replacement. Planning and design work is being actively pursued. A simplified flow-sheet of the plant is shown in Figs. 5 and 6. It hardly differs from the basic flow-sheet of the inactive pilot plant.

Facilities necessary for practical operation such as storage tanks for 1WW and MAW (medium-level waste) solutions, an evaporator for MAW and all devices needed for the handling of the glass blocks (quenching, sealing, etc.), have been added.

FIG. 6 FLOW SHEET II OF THE VETRIFICATION UNIT VERA 2

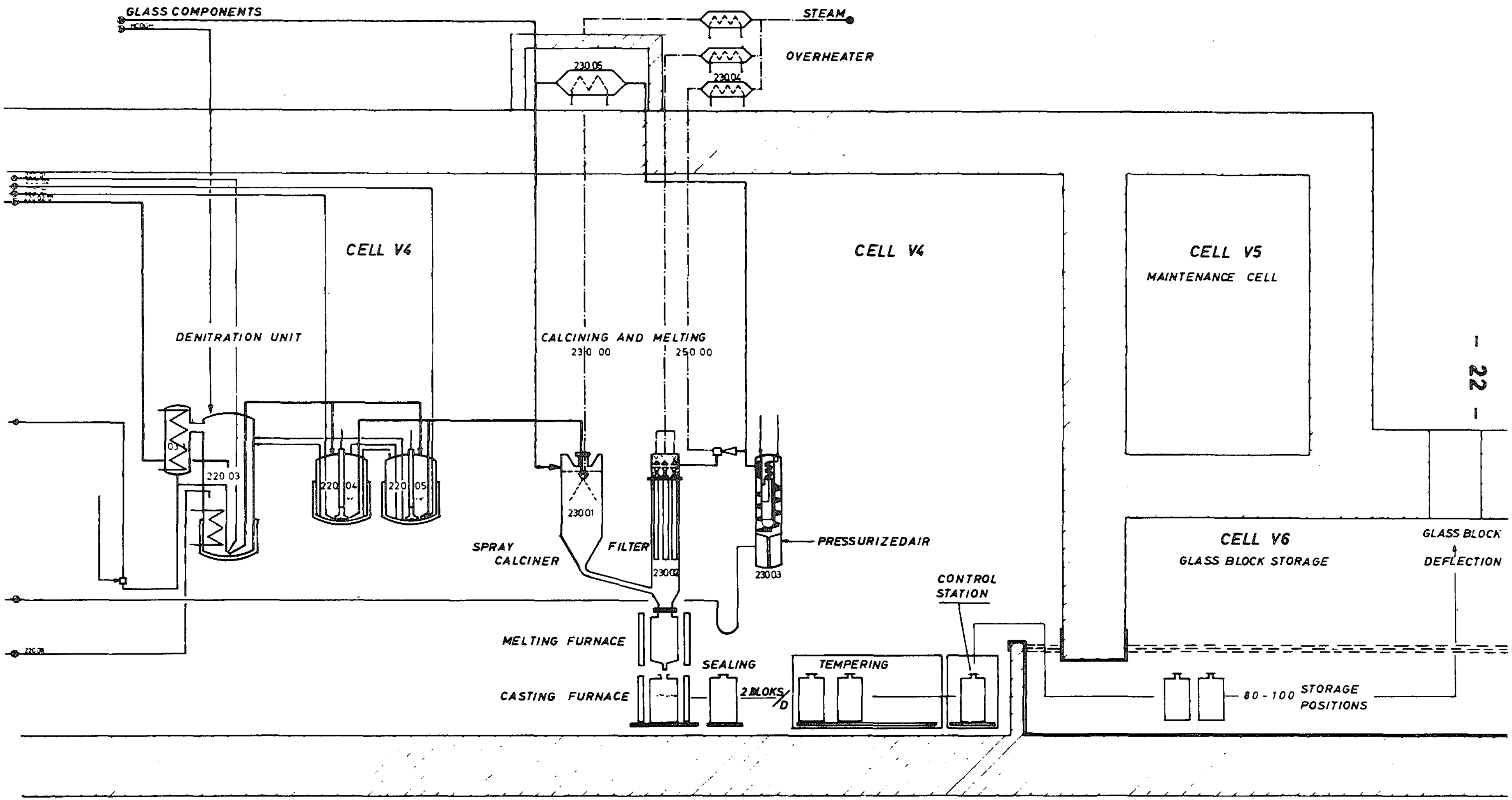
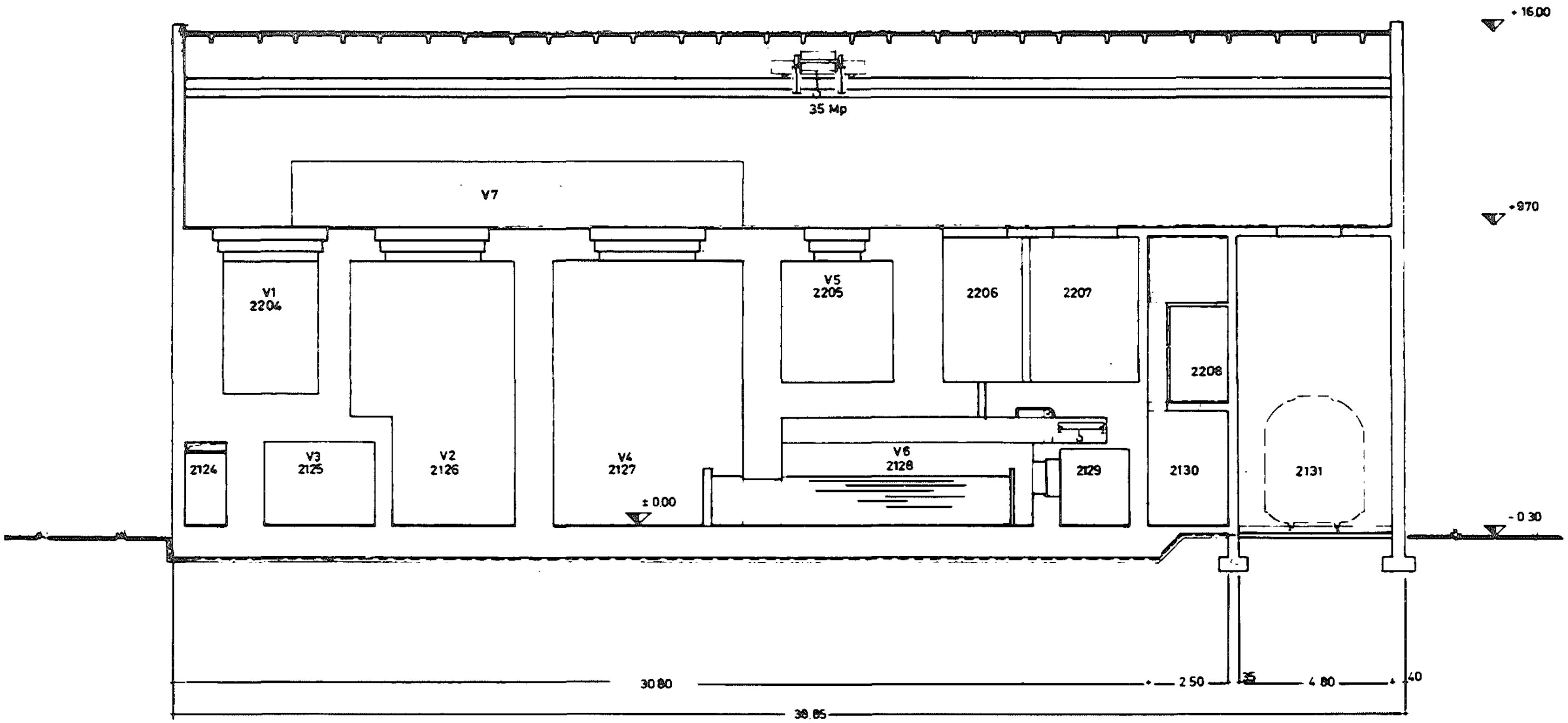


FIG. 7 LAYOUT OF THE VERA 2 BUILDING



M. 1:200

V1 IWW STORAGE
V2 OFF GAS CLEANING + MAW-EVAPORATOR
V3 MAW-STORAGE
V4 PROCESS CELL
V5 MAINTENANCE CELL
V6 GLASS BLOCK STORAGE
V7 OFF GAS FILTER ROOM

Fig. 7 shows the layout of the VERA 2 building which will be constructed on the WAK site north of the Karlsruhe Nuclear Research Center.

VERA 2 is designed for a throughput of about 5oo litres/d 1WW, i.e., a production of two 25 litres-glass blocks per day. To allow safe heat dissipation during storage in the Asse salt mine, the maximum heat production in the glass by radioactive decay is limited to 4o W/litre of glass, corresponding to an overall ß,γ-activity of approximately 25o,ooo Ci per glass block.

Construction work for VERA 2 is scheduled to start in spring 1973, highly active operation of the plant in late 1976.

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