KERNFORSCHUNGSZENTRUM

KARLSRUHE

Oktober 1974 KFK 2119

Abteilung Behandlung radioaktiver Abfälle

Bituminization of Radioactive Wastes at the Nuclear Research Center Karlsruhe

W. Bähr, W. Hild, W. Kluger

GESELLSCHAFT
FÜR
KERNFORSCHUNG M.B.H.

KARLSRUHE

GESELLSCHAFT FÜR KERNFORSCHUNG M. B. H.

KARLSRUHE

GESELLSCHAFT FÜR KERNFORSCHUNG MBH KARLSRUHE

KFK 2119

Bituminization of Radioactive Wastes at the Nuclear Research Center Karlsruhe

by

W. Bähr, W. Hild, W. Kluger
Abteilung Behandlung radioaktiver Abfälle

Paper presented at the 1974 Winter Meeting of the American Nuclear Society, Washington D.C.
Oct. 27 - 31, 1974

Abstract:

At the Karlsruhe Nuclear Research Center operation of the industrial bituminization plant for evaporator concentrates from low- and intermediate level radioactive effluents is flanked by R + D activities aiming both at the definition of operation conditions for the bituminization of other types of radwaste and at the investigation of related safety aspects. The essential part of the continuously operated industrial bituminization plant is a self-cleaning screw-extruder-evaporator. A 200°C steam heating allows the operation of the apparatus at a flexible temperature profile. Evaporation capacity is 140 kg H_2O/hr at very low residence times and low material hold-up. The apparatus is at the same time homogeneously mixing and coating the radioactive salt residues and efficiently evaporating the water contained in the evaporator concentrates. Since two years more than 1000 drums were filled with bitumen products, containing some 10^4 Ci FPs from more than 25000 m^3 low- and intermediate level radioactive effluents. A bench scale screw extruder unit of roughly 4 kg/hr evaporation capacity is operated at the R + D level. This unit guarantees the production of bitumen-products of exactly the same characteristics as those produced in the bituminization plant. This condition is essential for the performance of realistic investigations on bituminization and characterization of the resulting products. Apart from the determination of optimum operation conditions for concentrates containing chemically and thermally instable compounds, incorporation conditions for power reactor wastes have recently been established. At the same time investigations on the product characteristics (leaching, DTA-TGA, fire and explosion-hazard, fire fighting, etc.) are performed.

Both plant and R+D experience demonstrate that bituminization is a safe and effective means for the solidification of low- and intermediate level radwaste.

Zusammenfassung

Im Kernforschungszentrum Karlsruhe werden seit Anfang 1972 die Verdampferkonzentrate von schwach und mittelaktiven Abwässern in einer Bituminierungsanlage im technischen Maßstab zu einem endlagerfähigen Produkt verfestigt.

Der wesentliche Teil der kontinuierlich arbeitenden Anlage ist ein Doppelwellenextruder mit einer Ausdampfleistung von 140 l H_2O/h. Bisher wurden über 1000 Fässer mit einem Bitumen/Salzgemisch von je 50% und einigen 10^4 Ci Spalt- und Korrosionsprodukten abgefüllt. Die Anlage und einige Betriebserfahrungen werden beschrieben.

Neben der technischen Anlage ist eine kleine Versuchsanlage in Betrieb mit der alle Versuchs- und Entwicklungsprogramme für die Verfestigung von radioaktiven Rückständen in Bitumen durchgeführt werden können. Die Maschine hat eine Ausdampfleistung von 4 kg H_2O/h und garantiert Bitumenprodukte von gleicher Qualität und Beschaffenheit wie die einer technischen Anlage. An den Bitumenprodukten werden Auslaugrate, Feuer- und Explosionstests, Feuerbekämpfung, DTA-TGA usw. durchgeführt. Über die Ergebnisse wird berichtet.

Sowohl die Betriebs- als auch die Versuchsergebnisse zeigen, daß die Bituminierung ein sicheres und effektives Verfahren zur Verfestigung von schwach und mittelaktivem Radwaste, speziell aus Kernkraftwerken darstellt.

Bituminization of Radioactive Wastes at the Nuclear Research Center Karlsruhe

Since two years the concentrates from the evaporation of low- and intermediate level radioactive effluents produced in the various research institutes and reactors of the Nuclear Research Center Karlsruhe and in the 40 t/y reprocessing plant called WAK, are solidified by homogeneous incorporation into bitumen at the waste treatment facilities of the Center. This solidification technique has successfully replaced the solidification by mixing cement that had been applied till that time. As shown in figure 1 bituminization leads to a solidified waste that is roughly 5 times smaller in volume than that obtained by concreting; furthermore the leach rates of bitumen products are generally two orders of magnitude lower than those of concreted wastes.

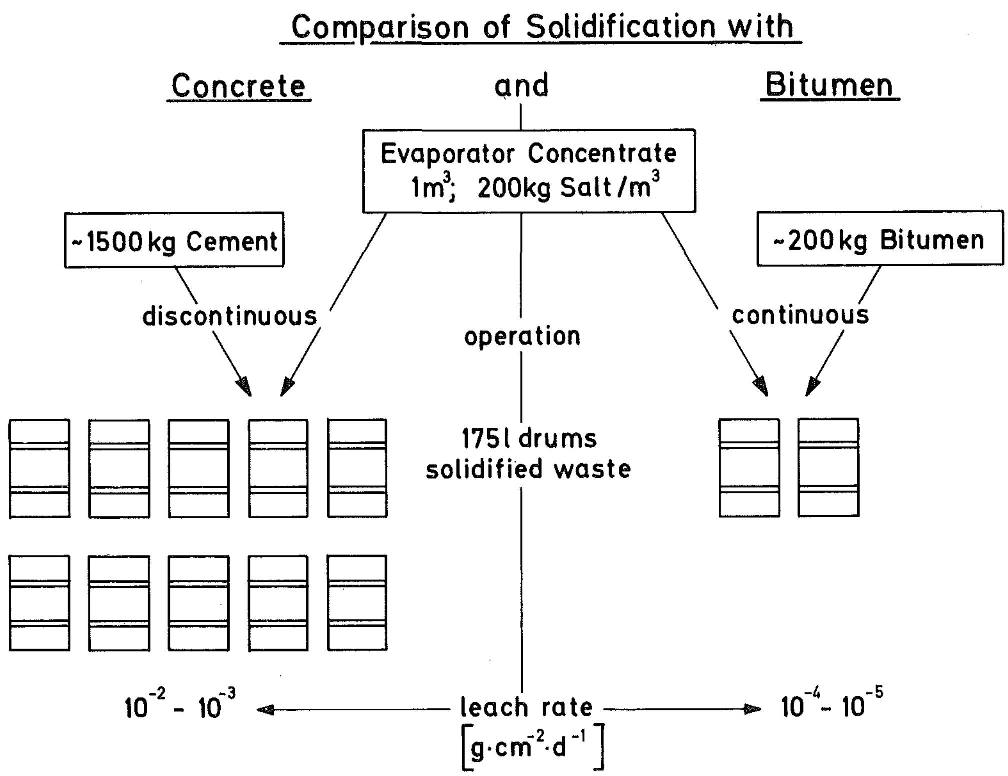
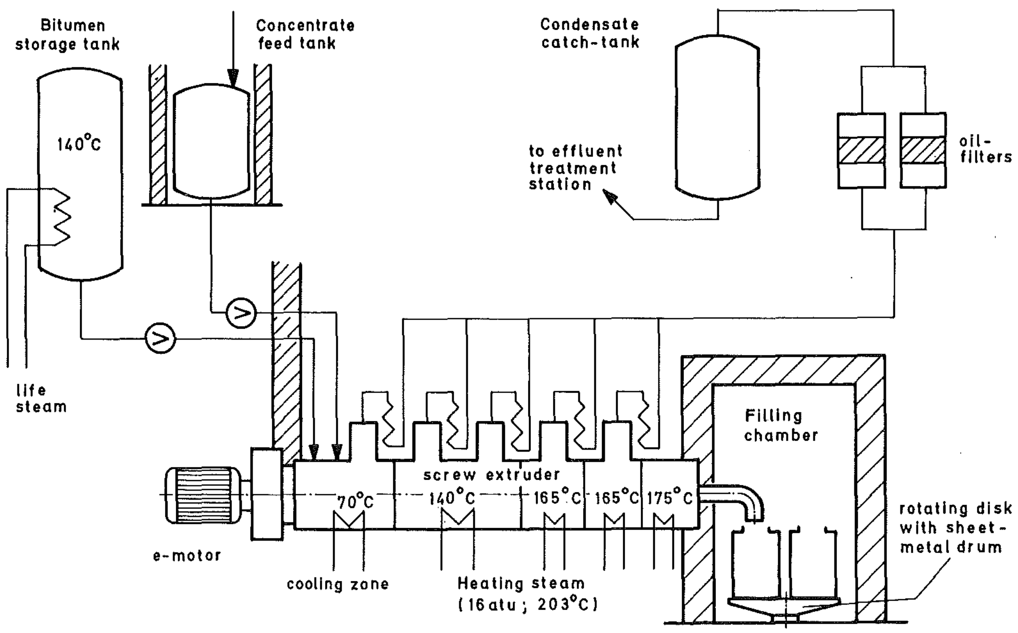


Fig. 1

A simplified functunal flowsheet of the bitumen plant is shown in figure 2. As demonstrated incorporation into bitumen is performed in a self-cleaning screw-extruder. Liquid bitumen that is stored at 140°C is fed to the extruder together with evaporator concentrate, the P_H of which has been adjusted between 8 and 10. At the temperature profile stated, the water is evaporated and the radioactive residues are coated with bitumen. The evaporated water is condensed, passed over an oil filter and recycled to the effluent treatment station. An extremely homogeneous bitumen product flows into a 175 l sheet-metal drum standing on a turntable that holds 6 drums. Filling of each drum is performed in 3 stages to allow for volume contraction during cooling. After 24 hours total cooling time the filled drums receive a loose cover and are placed into a 200 l reinforced drum that is transported by railway to the Asse salt mine in special reusable shielded transport containers. Another possibility is the insertion into prefabricated concrete containers which are closed by pouring a concrete lid.



Simplified functional Flowsheet

Fig. 2

Figure 3 shows the flowsheet representing normal plant operation. At a feed rate of roughly 150 l/h evaporator concentrate the screw-extruder operates at optimum evaporation capacity of ~ 140kg H_2O/h yielding a bitumen product that contains 50 wt% salt with $<$ 0.5 wt% residual water.

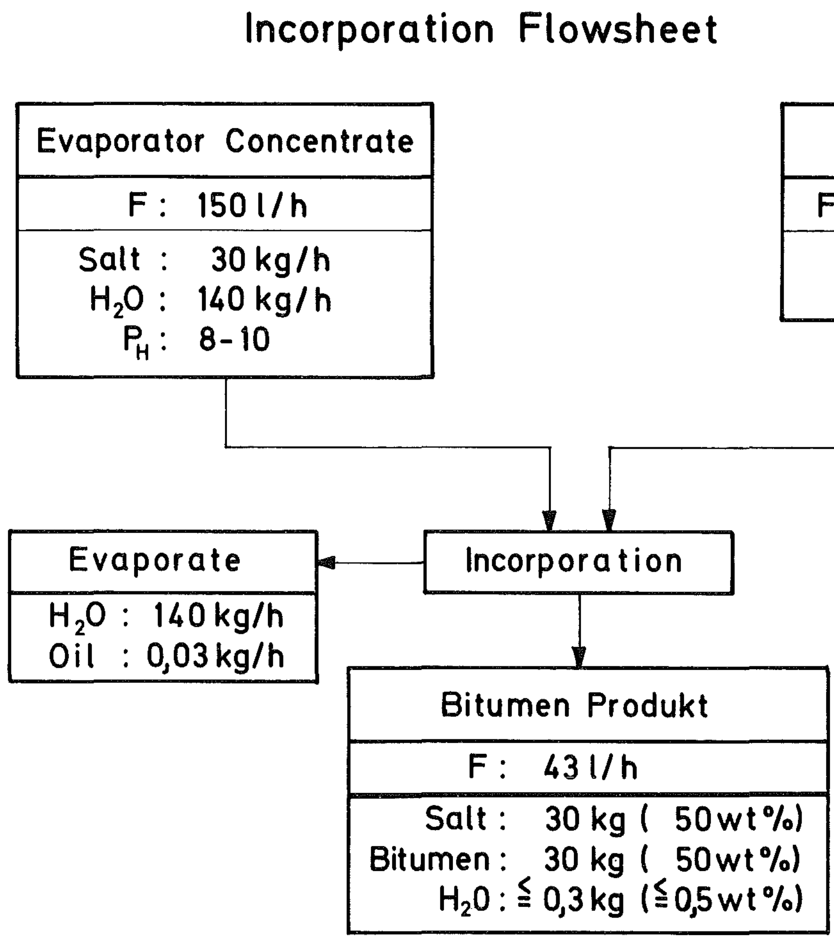


Fig. 3

Figure 4 shows a bitumen product containing 65% wt salt.

Fig. 4

Figure 5 shows the ZDS-T 120 screw-extruder of the bituminization plant during installation.

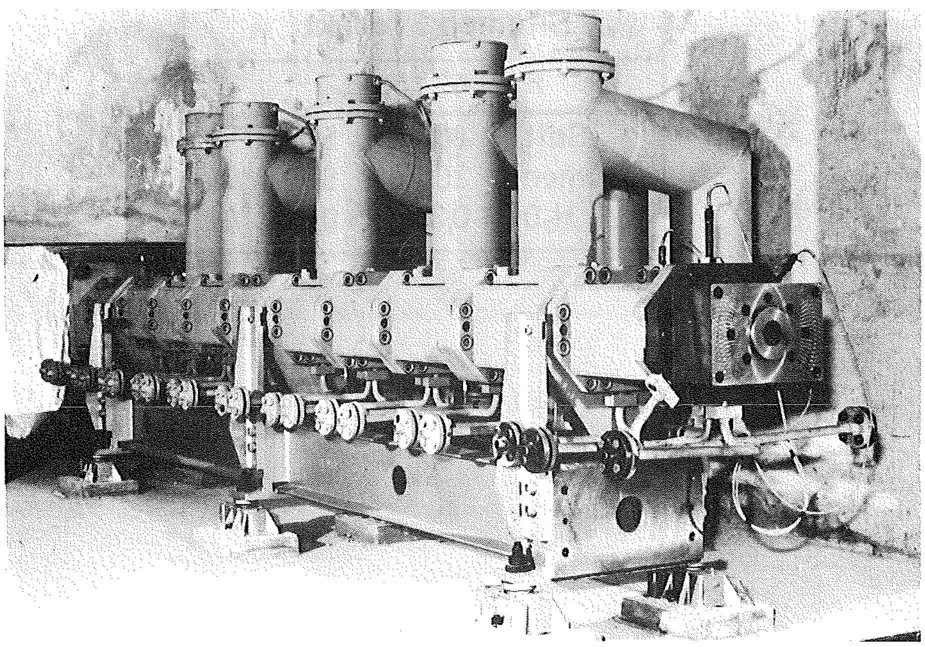


Fig. 5

This screw-extruder, manufactured by Werner & Pfleiderer for heavy duty plastic processing, has in cooperation with the Waste Management Department of the Nuclear Research Center Karlsruhe especially been adapted for the incorporation of radioactive waste into bitumen.

It is mainly characterized:

- by a special pair of self-cleaning screws that provide both forced transport and intensive mixing and kneading.
- by 5 steam-heated zones with independent temperature regulation for the selection of an appropriate temperature profile and
- by very low material hold-up of a few liters and residence time of 2 to 3 minutes.

Thus an effective evaporation and an extremely homogeneous incorporation of the waste residues into bitumen is guaranteed at rather gentle treatment of the material and a high degree of flexibility.

Since start-up of the plant in 1972 evaporator concentrates from more than 25000 m^3 low- and intermediate level radioactive effluents containing some 10^4 Ci of fission products were successfully solidified in the bitumen plant yielding roughly 1100 drums. Average specific activity of the solidified waste amounted to 0,1 Ci/l, occasionally products of up to 0.5 Ci/l were obtained.

During more than two years satisfying plant operation the screw-extruder proved to be a reliable and safe equipment.

Figure 6 shows the direct current geared motor that drives the screw-extruder; the screw speed is variable between 0 and 300 revolutions/min.

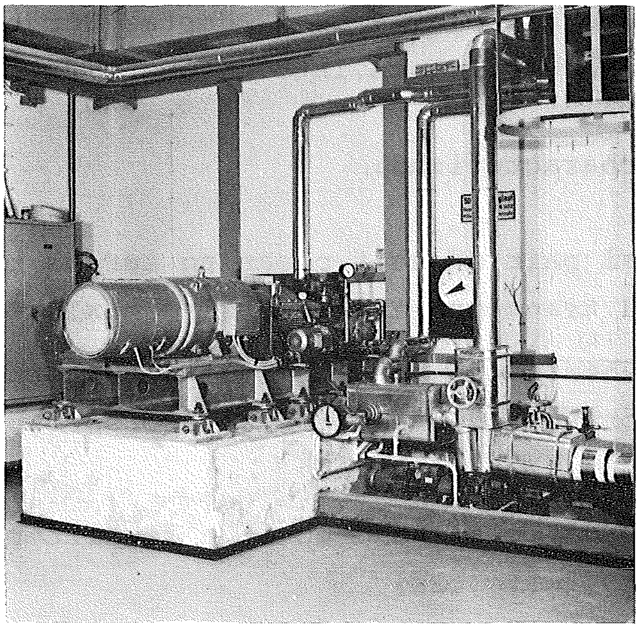


Fig. 6

Figure 7 shows a view into the filling chamber, where the bitumen product that flows into the drum can be seen.

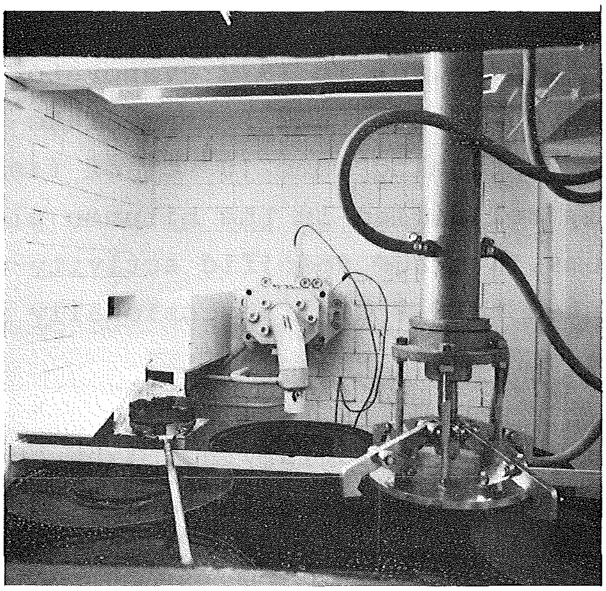


Fig. 7

Figure 8 shows the removal of filled drum from the filling chamber.

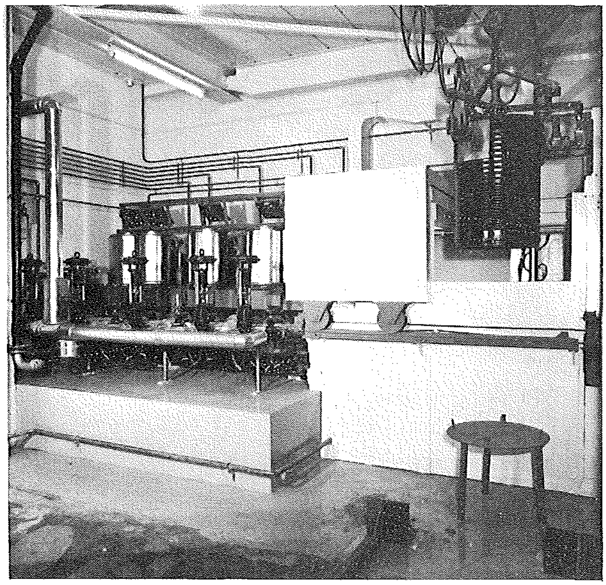


Fig. 8

Figure 9 shows pre-fabricated concrete-containers for shipping and storage.

Fig. 9

Figure 10 shows the containers after being topped of with concrete, ready for shipment by railway to the Asse-salt mine.

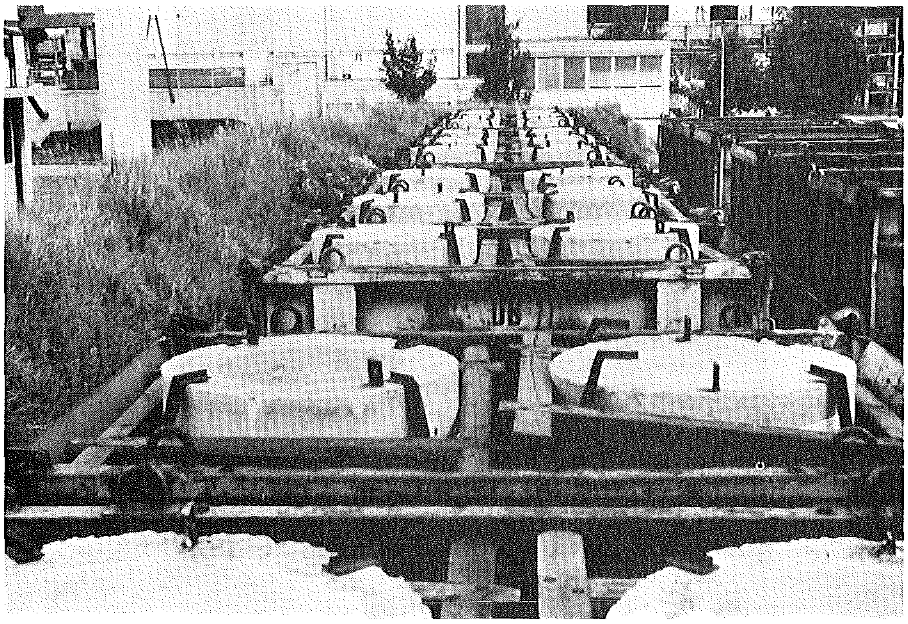


Fig. 10

Figure 11 shows a reusable shielded transport container for 1 drum

Fig. 11

Figure 12 shows a shielded transport container for 7 drums.

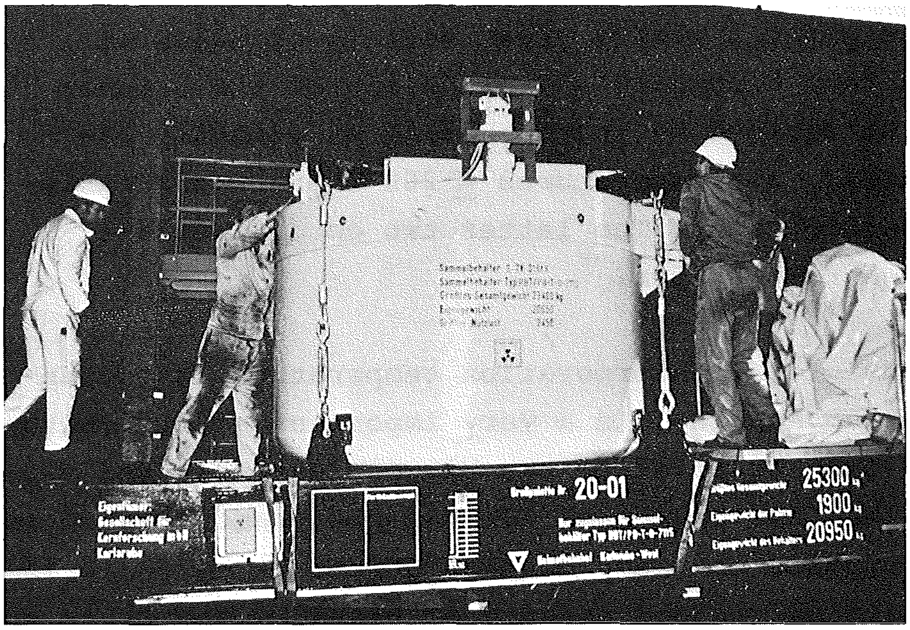


Fig. 12

These containers are designed for different levels of activity.

Both the conception of the bituminization plant and the definition of the operation conditions were based on the results of extensive R + D work. The bitumen selected for the plant is a Mexphalt 15 or Ebano 15 medium-hard distilled bitumen of 67 to 72°C ring and ball softening point and a penetration of 10 to 20.

Due to the fact that approximately 1/3 of the low-level effluents (average specific acticity 10^{-2} Ci/m^3) and more than 80% of the intermediate level effluents (up till 100 Ci/m^3) result from the reprocessing plant, rather high $NaNO_3$ concentrations were expected. Actually up till 70wt% of the salts is $NaNO_3$.

The problem of bitumen oxidation and hardening was thus thoroughly investigated. From the results of these extensive investigations with a great variety of salts it was concluded that hardening and oxidation of the bitumen could safely be avoided by incorporating at slightly alcaline conditions, at temperatures $\leq 200^{o}C$ and preferrably at short residence times. The latter two conditions are best met in a scre-extruder.

The limitations of the incorporation temperature as guaranteed by the steam heating, is a very important safety factor as far as the burning point of the bitumen products and exothermal reactions are concerned. It had been demonstrated in numerous experiments that the burning points of Mexphalt 15 products containing various amounts of nitrates and other compounds expected in the evaporator concentrates were generally higher than $300^{o}C$, thus leaving a safety margin of at least $100^{o}C$ during incorporation. An exhaustive investigation performed at the Institute of the Chemistry of Propellants and Explosives demonstrated clearly that bitumen products containing 60 wt% $NaNO_3$ can neither be classified as an explosive nor exploded by shock waves. Fire tests performed with bitumen products containing up to 50 wt% $NaNO_3$, showed that the products cannot be considered easily flammable. Fire-fighting is best with CO_2 as demonstrated in the following figures.

Figure 13 shows a 175 l sheet-metal drum containing bitumen product of 42 wt% $NaNO_3$ inserted into a trough with a light fuel that is ignited.

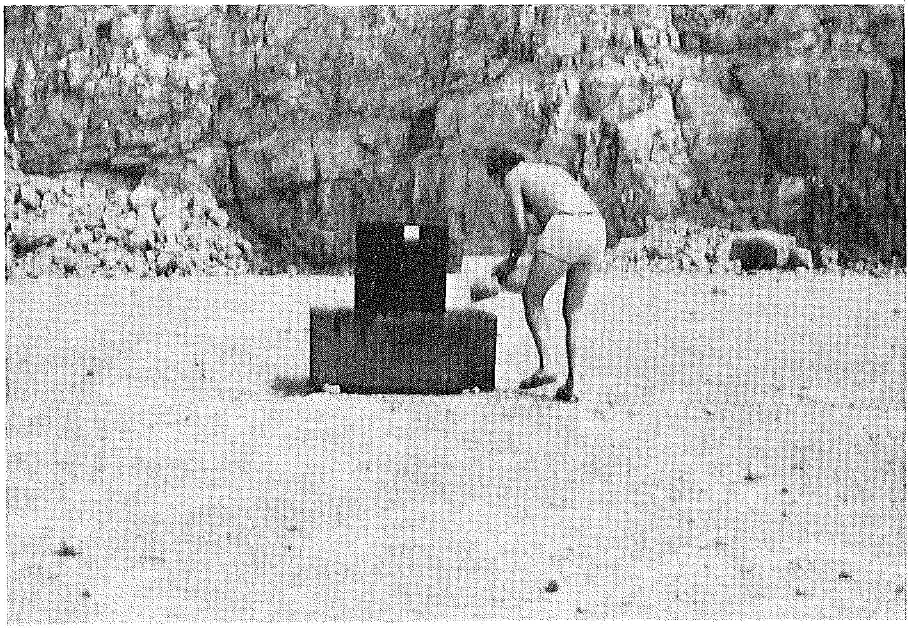


Fig. 13

Figure 14 shows the drum 15 minutes after ignition.

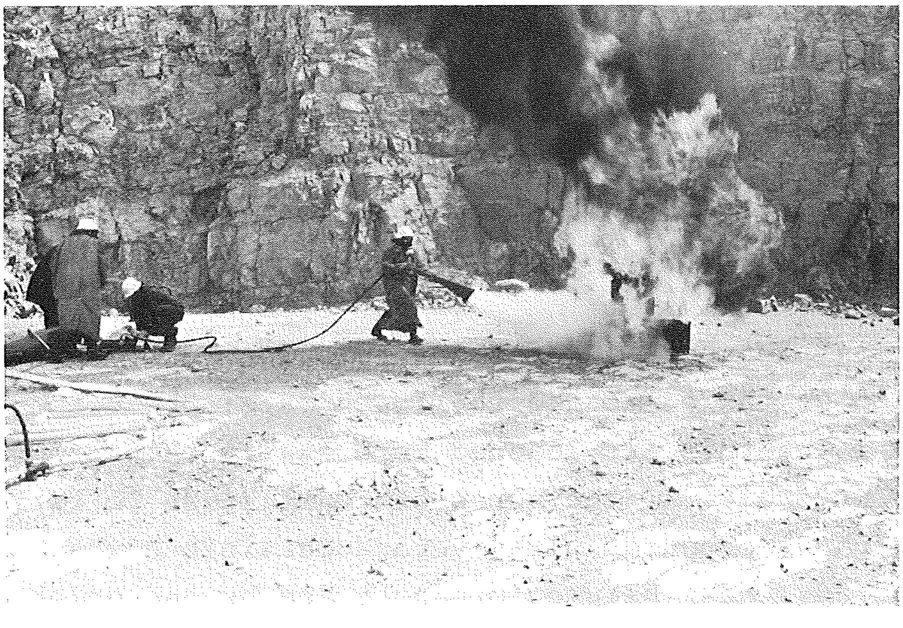


Fig. 14

Figure 15 shows the fire brigade that extinguished the fire by CO_2 in less than 1 minute.

Fig. 15

Extensive leaching tests were performed with various simulated waste products. Figure 16 shows a direct dependence of the leach rate from the salt concentration.

Products of high salt content, coated with a layer of 5 mm pure bitumen were completely resistent to leaching over a period of 2 1/2 years.

Figure 17 shows an interesting relation between the dispersion of the salts and the leach rate: products with coarser crystals are leached more easily than products with finer crystals. As the screw-extruder leads to extremely homogeneous products with average particle sizes between 10 and 30μ these bitumen products are by one order of magnitude less leachable than comparable products from pot processes.

Leaching rates of bitumen-$NaNO_3$ mixtures vs. salt content (bitumen: Mexphalt 15)

The leaching rate are mean values over the entire observation period (1year)

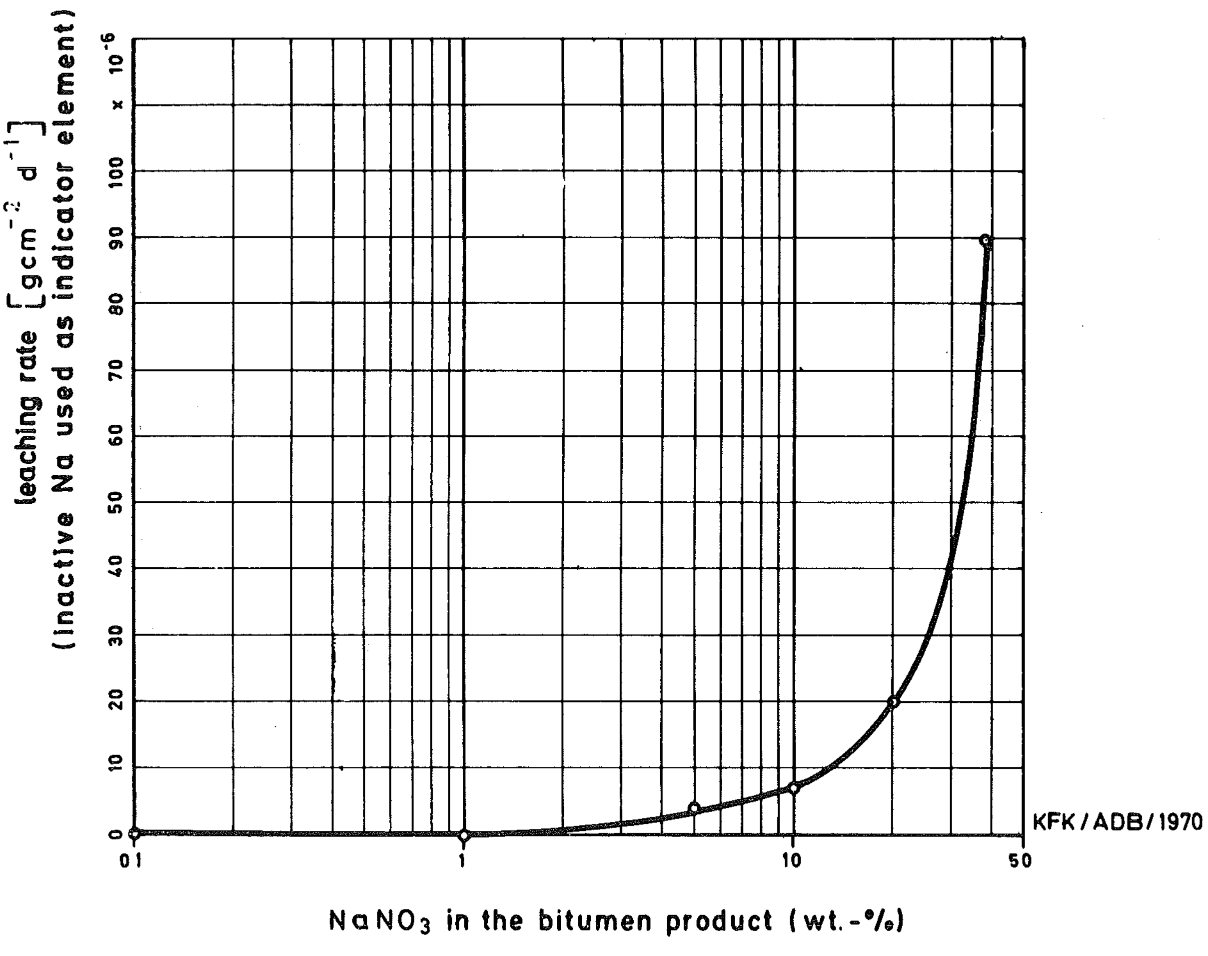


Fig. 16

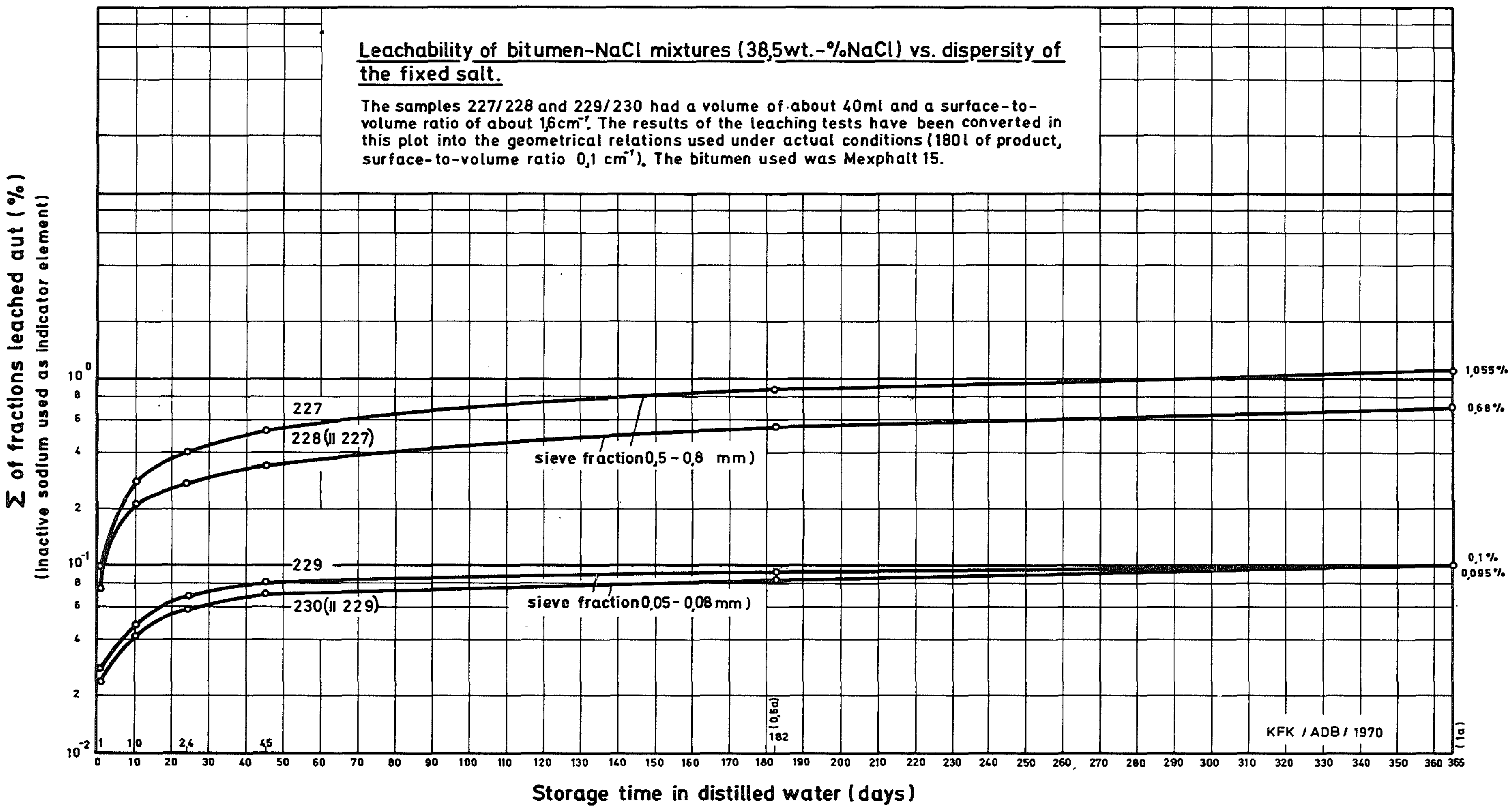

Leachability of bitumen-NaCl mixtures (38,5wt.-%NaCl) vs. dispersity of the fixed salt.
The samples 227/228 and 229/230 had a volume of about 40ml and a surface-to-volume ratio of about 1,6cm⁻¹. The results of the leaching tests have been converted in this plot into the geometrical relations used under actual conditions (180 l of product, surface-to-volume ratio 0,1 cm⁻¹). The bitumen used was Mexphalt 15.
Σ of fractions leached out (%)
(inactive sodium used as indicator element)
227
228(II 227)
sieve fraction 0,5 - 0,8 mm)
229
230(II 229)
sieve fraction 0,05 - 0,08 mm)
1,055%
0,68%
0,1%
0,095%
(0,5a)
182
(1a)
KFK / ADB / 1970
Storage time in distilled water (days)

Fig. 17

Figure 18 shows the porosity $(\varepsilon = 1 - \frac{\rho'}{\rho})$ +) of a bitumen product from the screw extruder containing 42 wt% $NaNO_3$ as a function of the absorbed dose of an 10 MeV electron irradiation.

It results that 0,6 vol% 22 vol% and until 40 vol% porosity occurs after irradiation to 10 Mrad, 100 Mrad and 500 Mrad respectively. In further irradiation experiments a direct proportionality was found between the radiolytic Hydrogen - production and the total absorbed dose. A hydrogen formation rate between 0.4 and 0.5 ml Hydrogen/g product and 100 Mrad was found for the above product at 10 MeV electron irradiation and γ-irradiation in a fuel element storage pond. This value is of importance for safety considerations in connection with the disposal. A special calculation program is actually under way for the determination of threshold conditions for the perpetual storage of solidified waste in salt caverns of given diameter.

Actual R+D activities aim at an improvement of the plant operation by trouble shooting, at the definition of operation conditions for the bituminization of other types of radioactive waste and at the investigations of related safety aspects.

Figure 19 shows the bench scale screw-extruder of roughly 4 kg/h evaporation capacity. This unit guarantees the production of bitumen products of exactly the same characteristics as those obtained in the large plant. This is an essential condition for the performance of realistic investigations.

+) ρ' = density after irradiation
   ρ = density before irradiation

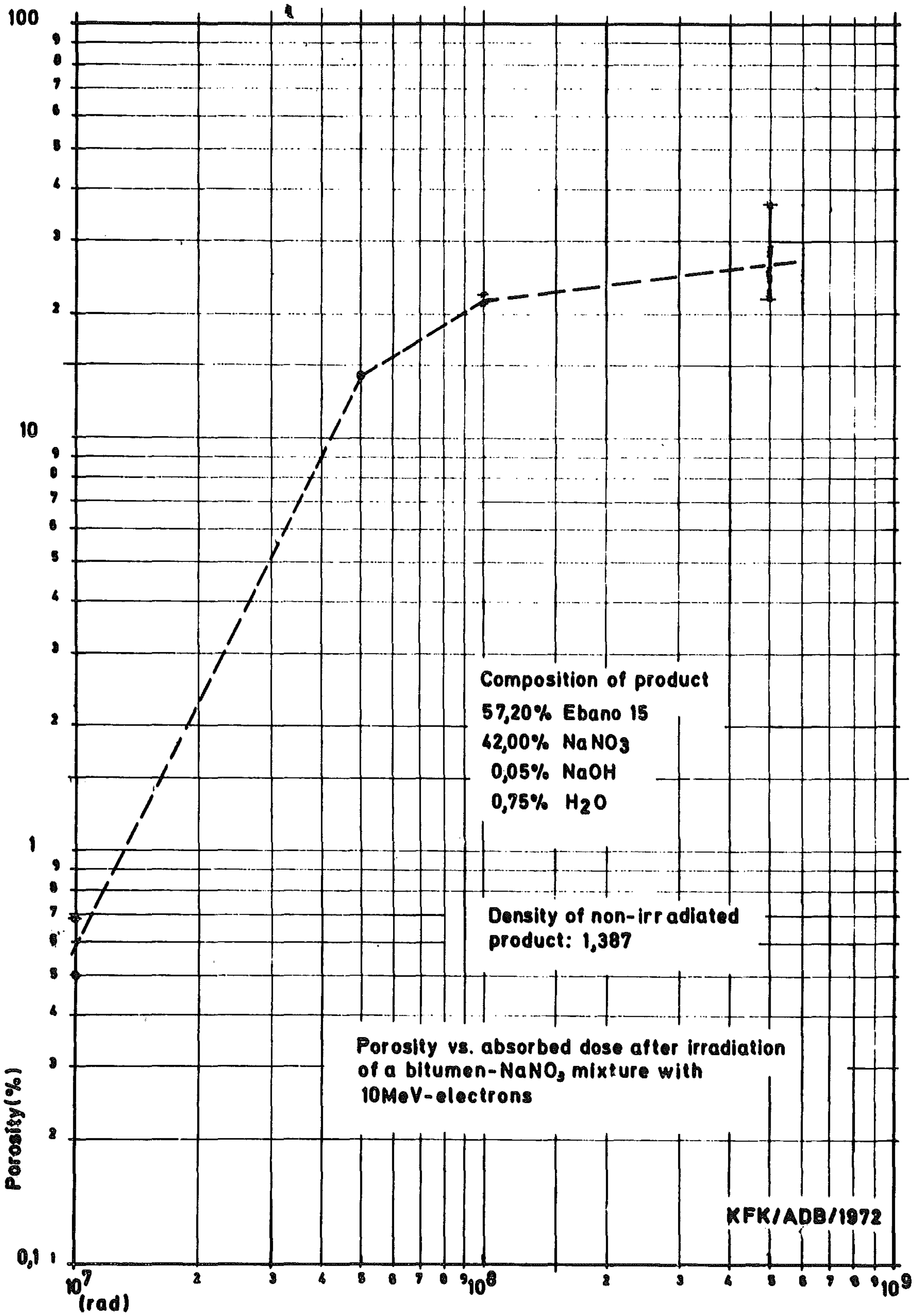

100
10
1
0,1
Porosity (%)
10^7 (rad)
10^8
10^9
Composition of product
57,20% Ebano 15
42,00% $NaNO_3$
0,05% NaOH
0,75% H_2O
Density of non-irradiated product: 1,387
Porosity vs. absorbed dose after irradiation of a bitumen-$NaNO_3$ mixture with 10MeV-electrons
KFK/ADB/1972

Fig. 18

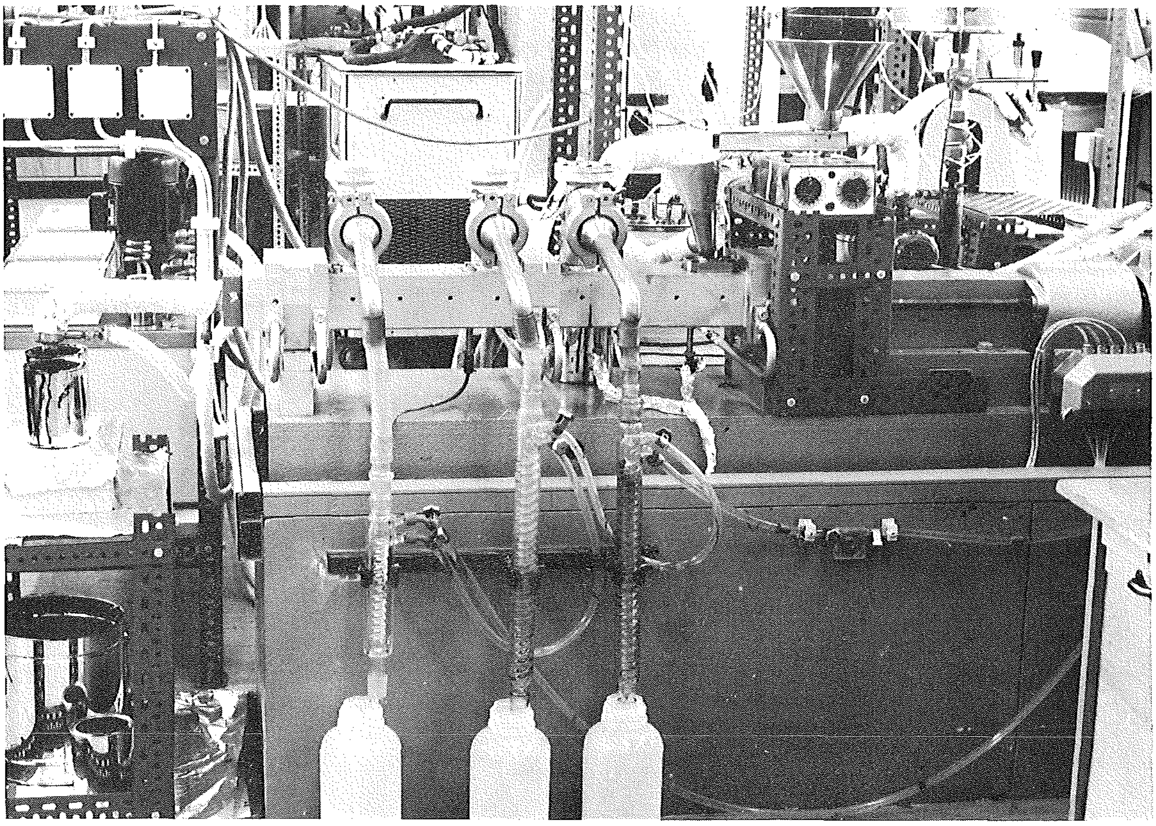


Fig. 19

Trouble-shooting-investigations were performed in connection with two incidents that occured during plant operation.

In the first case the final fraction of the feed tank was not agitated and contained a large amount of PVC-powder, that - as it turned out later - is a filler in pickling pastes used for decontamination and that floats on the surface of evaporator concentrate. The drum receiving the slightly foaming bitumen product of about 200°C was in contrast to the operation instructions not allowed to cool down during 24 hours but immediately inserted into a 200 l reinforced drum. This assembly acted as a thermostate and the PVC decomposed yielding Hcl that most probably initiated an oxydation of the organic material by decomposing nitrates. Although the escaping fumes set an alarm no fire occured. Apart from the sealing no damage was detected at the reinforced drum and the incident had no influence on the other drums stored in the immediate vicinity.

Figure 20 shows a view into the storage cell after the incident.

Fig. 20

The second incident was also brought about by the coincidence of two sources of error.

First the failure of the agitator in the evaporator concentrate tank resulted obviously in a serious inhomogenity of the aqueous feed. The incident happened when starting the incorporation of a new charge of evaporator concentrate that due to a maloperation was 1 molar in NaOH (P_H = 13,8).

The bitumen product was foaming and unnormal fumes were detected in the filling chamber. Suddenly the fumes caught fire, as a consequence of which the two drums that had received fractions of the corresponding bitumen product caught fire too. The other 4 drums did not burn. The fire was easily extinguished with CO_2. Practically no damage was caused in the filling chamber and no persons were injured. As the flash-fire occured in the gas phase, only very little room contamination was found.

This incident is most probably due to the decomposition of accumulated organic compounds into easily flammable volatile compounds at the high alcalinity. The investigations demonstrated that such compounds are for instance the antifoaming agents utilised during evaporation, TBP and its degradation products from reprocessing, adducts of polyethyleneoxide utilised in decontamination solutions etc.

Furthermore when incorporated at the high alcalinity the resulting bitumen products have burning points around 200°C. When incorporated at P_H 8 to 10 however, no degradation occurs and burning points of the resulting products are in the region of 400°C. After appropriate P_H adjustment with H_3PO_4 the remaining evaporator concentrates were incorporated without any difficulty.

A couple of additional control and safety measures have been adopted as a consequence of this incident and the plant has continued successful and safe operation.

Power reactor wastes are rather clean wastes compared to the extremely complex composition of the evaporator concentrates incorporated at Karlsruhe. As they are practically free of nitrates and organic compounds coming from reprocessing, incorporation of power reactors wastes into bitumen is undoubtedly a very attractive solidification procedure. This is not only true for the chemical composition but also for the activity of these wastes. Regardless whether sludges from a chemical effluent by precipitation or concentrates from an evaporation have to be solidified, homogeneous incorporation into bitumen by means of a screw extruder is a reliable and safe technique. Furthermore incorporation conditions for spent mixed bed ion exchangers saturated with Li and boric acid yielding bitumen products of up to 50 wt% ion exchanger were determined and successfully demonstrated in the bench-scale unit.

In concluding that brief summary it can be said that both, plant and R + D experience demonstrate that bituminization is a safe and effective means for the solidification of low and intermediate level radioactive waste. Screw-extruders of the Werner & Pfleiderer type proved to be very reliable and flexible for continuous incorporation to extremely homogeneous products. There is no doubt that this process technique is ideally suited for the safe solidification of power reactor wastes and will thus find a broad application in the future.

References

1.) Jahresbericht 1967 der ASD/D, KFK-888, S. 49

2.) Jahresbericht 1968 der ADB, KFK-1030, S. 43

3.) Jahresbericht 1969 der ADB, KFK-1346, S. 16

4.) Jahresbericht 1970 der ADB, KFK 1500, S.9

5.) Jahresbericht 1971 der ADB, KFK-1830, S. 7

6.) Jahresbericht 1972 der ADB, KFK-2000, S. 7

7.) Jahresbericht 1973 der ADB, KFK-2126, im Druck

8.) Jahresbericht 1974 der ABRA, in Vorbereitung

9.) W. Kluger, H. Krause, O. Nentwich, "Fixing of Radioactive Residues in Bitumen" KFK-1037 (1969)

10.) "Bituminization of Radioactive Wastes" Technical Reports Series No. 116, IAEA Vienna STI/DOC/10/116 (1970)

11.) W. Bähr, W. Hempelmann, H. Krause, O. Nentwich " Experiences in the Treatment of Low-and Intermediate Level Radioactive Wastes in the Nuclear Research Center Karlsruhe" IAEA-SM-137/12, S. 471

12.) H. Krause, R. Randl " Treatment and Final Disposal of Radioactive Wastes from Fuel Reprocessing in the Federal Republik of Germany - a Survey on Policy and R+D Work". Management of Radioactive Wastes from Fuel Reprocessing (Proc. Symp. Paris 1972) OECD, Paris 1973, S. 199 Siehe auch KFK-1741.

13.) E. Backof, W. Diepold
"Untersuchungen über die thermische und mechanische Empfindlichkeit von Bitumen/Sauerstoffgemischen"
Institut für Chemie der Treib-und Explosivstoffe, Berghausen/Karlsruhe, Technische Mitteilung Nr. 9/70 (1970).

14.) W. Bähr, G. Meier
"Die Anlage zur Fixierung radioaktiver Verdampfer-konzentrate in Bitumen im Kernforschungszentrum Karlsruhe
KFK 2104

15.) IAEA Waste Management Research Abstracts
Nr. 4 p. 69-70 1968

16.) IAEA Waste Management Research Abstracts
Nr. 6 p. 74-75 1971

17.) IAEA Waste Management Research Abstracts
Nr. 7 p. 26-27 1972

18.) IAEA Waste Management Reseach Abstracts
Nr. 8 p. 82 1973

19.) IAEA Waste Management Research Abstracts
Nr. 9 p. 43 and p. 55-56 1974