KERNFORSCHUNGSZENTRUM

KARLSRUHE

Mai 1976 KFK 2328

Abteilung Behandlung radioaktiver Abfälle

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PWA-Nr. 44/76

Bituminization of Radioactive Wastes at the Nuclear Research Center Karlsruhe - Experience from Plant Operation and Development Work *)

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*) Paper presented at the NEA Seminar on the Bituminization of Low and Medium Level Radioactive Wastes, Antwerp, 18 - 19th May 1976

Abstract

A summary is given of the main operational experience gained at the Nuclear Research Center Karlsruhe in 4 years operation of the bituminization plant for evaporator concentrates from low- and medium level wastes. At the same time some of the essential results are compiled that have been obtained in the R+D activities on bituminization.

Kurzfassung

Bituminierung radioaktiver Abfälle im Kernforschungszentrum Karlsruhe - Betriebserfahrungen und Entwicklungsarbeiten

Es wird eine Zusammenfassung über die wesentlichen Betriebserfahrungen gegeben, die im Kernforschungszentrum Karlsruhe in 4 Jahren bei der Bituminierung von schwach- und mittelaktiven Verdampferkonzentraten gesammelt wurden. Gleichzeitig werden auch die wichtigsten Ergebnisse zusammengefaßt, die in den auf dem Gebiet der Verfestigung von radioaktiven Abfällen in Bitumen durchgeführten Forschungs- und Entwicklungsarbeiten erzielt wurden.

Résumé

Bituminization des déchets radioactifs au Centre des Recherches Nucléaires à Karlsruhe - Expériences des installations et travaux de développement

Un résumé est donné sur les principales expériences operationelles obtenues au Centre de Recherches Nucléaires de Karlsruhe en 4 années d'operation sur la bituminisation des concentrats d évaporation des effluents de faible et moyenne activité. En même temps on présente quelques résultats essentiels obtenus sur les activités de recherche et de développement de l'enrobage des déchets radioactifs en bitume.

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1. INTRODUCTION

Due to the very restrictive activity discharge limits, allowing release of liquid effluents to the main canal only after decontamination to activity concentration equal to drinking water standards for occupationally exposed personnel, efficient waste treatment techniques had to be selected for the Nuclear Research Center Karlsruhe. Evaporation of low and medium level waste streams turned out to be the most effective and most economic procedure from various liquid waste treatment processes tested on a pilot scale in the early sixties and has thus been adopted in a large treatment plant starting operation in 1968 {1}.

The evaporator concentrates from that plant were solidified during the first years by mixing with concrete. This batchwise operated solidification technique has successfully been replaced by the continuous bituminization process in 1972. The plant, the essential part of which is a self-cleaning screw-extruder evaporator, allows at the same time the effective evaporation of the water from the evaporator concentrates and the homogeneous incorporation of the radioactive salt residues into bitumen.

In comparison with the solidification by mixing with concrete incorporation into bitumen has - among others - the following main advantages

- the volume of the solidified waste that has to be stored perpetually is roughly 5 times smaller, and
- the leach rates of the bitumen products are generally two orders of magnitude lower.

The selection of the process type installed in the waste treatment facilities at Karlsruhe was based both on R+D-work that started in 1964 comprising lab-scale investigations and process engineering tests and on the evaluation of bituminization experience collected elsewhere {1}. Emphasis was given mainly to the definition and evaluation of process and product data relevant to the safe incorporation of the evaporator concentrates typical for the Research Center and to the safe intermediate storage, transport and final disposal in the salt mine Asse of the resulting bituminised waste products.

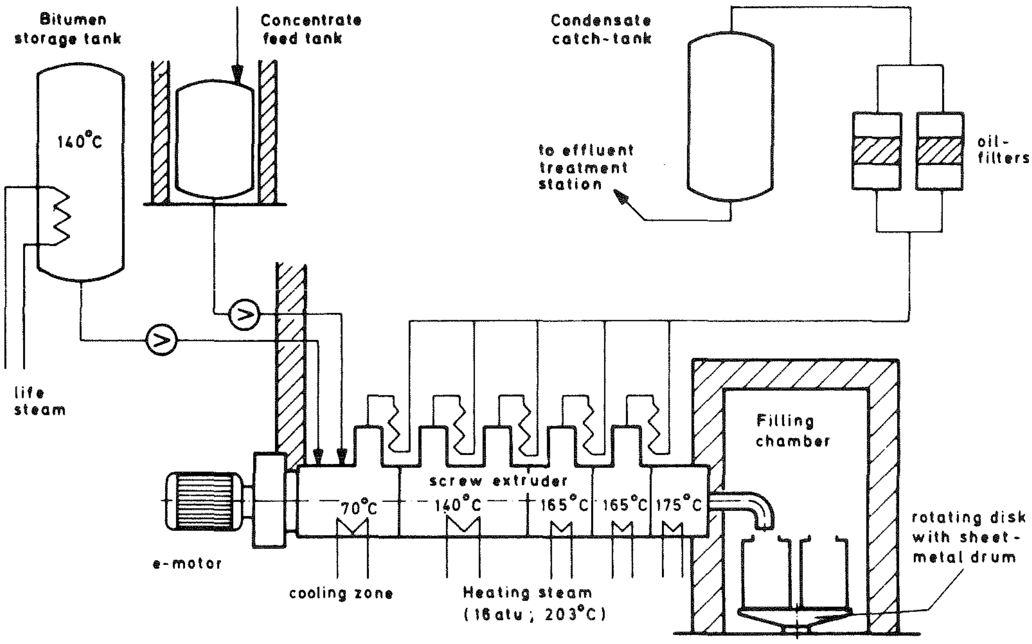
Operation of the industrial bituminisation plant is still flanked by R+D activities aiming both at the definition of operation conditions for the bituminization of other types of radwaste and at the investigation of related safety aspects. To this end and for trouble shooting experiments a bench scale screw extruder unit is operated too, that guarantees realistic incorporation experiments yielding bitumen products of exactly the same characteristics as those produced in the bituminization plant. This condition is essential for the practical application of the experimental results obtained.

This paper is an attempt to summarize some of the essential experience and results gained in radwaste bituminization at Karlsruhe both in plant operation and R+D activities.

2. PLANT OPERATION

2.1 Description of the bituminization plant

A detailed description of the bituminization plant, that has been installed in existing rooms of the waste treatment facilities, is given in reference {2}. For convenience figure 1 shows a simplified functional flowsheet. Bituminization occurs in a Werner & Pfleiderer type ZDS-T 120 extruder evaporator, with a pair



Simplified functional Flowsheet

Figure 1

of intermeshing screws of self-cleaning profile. Liquid standard grade Mexphalt 15 bitumen that is stored at 140^oC in a 20 m^3 tank is fed to the extruder together with evaporator concentrate from the shielded 1 m^3 concentrate feed tank. At the typical temperature profile stated evaporation of water and incorporation of the radioactive residues takes place simultaneously. After condensation the water passes an oilfilter and is recycled to the effluent evaporator. The bitumen product flows into one of six 175 l sheet-metal drums standing on a turntable in the filling chamber. Extruder and bitumen tank are heated by steam.

It should be noted that this plant was the first plant utilising this particular technology for the direct bituminization of evaporator concentrates with up till 70 wt.% of the contained salts being $NaNO_3$.

2.2 Plant performance

Figure 2 shows the flowsheet representing normal plant operation, with the screw extruder working at optimum evaporation capacity of roughly 140 kg H_2O/h yielding an extremely homogeneous bitumen product of 50 wt.% salt with $\leq$ 0.5 wt.% residual water. The PH of the evaporator concentrate has to be adjusted between 8 and 10.

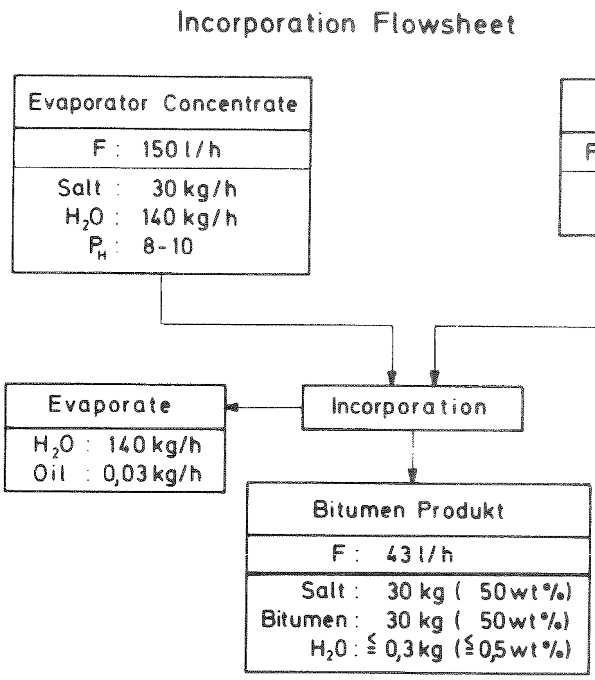


Figure 2

Since start-up of the plant in 1972 roughly 700 m^3 of evaporator concentrates from more than 40,000 m^3 low and intermediate level effluents produced in the Center and the 40 t/y reprocessing plant WAK were solidified by incorporating the solid residues containing some 10^4 Curies into bitumen. Approximately 2000 drums were produced with an average specific activity of 100 Ci/m^3 and 50 wt.% salt content and were shipped to the Asse salt mine for disposal. Distribution of dose rates was as follows: roughly 50%, 30% 10% and 5% of the drums had surface dose rates of up to 20, 40, 60 and 80 R/h, respectively; whereas the rest showed dose rates up till 200 R/h. To cope with this the sheet-metal drums were either placed into a 200 l reinforced drum that was inserted in special reusable shielded transport containers or the sheet-metal drums were inserted into prefabricated concrete containers which after being topped of with concrete were transported to the Asse for disposal.

From the operation experience that is described in detail in references {2,3} let us cite only the following points:

Bitumen losses and coking problems known from bitumen storage at ≥ 200°C in refineries were not observed in the bitumen storage tank (140°C). The strainer in front of the bitumen metering pump becomes mainly clogged by coking sediments one day after recharging the bitumen tank.

Sedimentations of salt and bitumen salt mixes occasionally occurred at the steam domes but could successfully be cleaned by a specially developed cleaning system operating with steam jets.

To cope with the volume contraction upon cooling and to provide for better cooling during filling the 6 drums on the turntable are filled successively for approximately 30 minutes each, and are then changed. Thus a drum is filled after 9 to 10 changes. After an additionary cooling period of about 24 hours when the centerline temperature of the products has dropped to $\leq$ 110°C the drums are transferred to the interim storage area. The outside of the sheet metal drums contains always some quite adhering contamination, which is not eliminated as the drums are anyhow inserted into a second container (reinforced steel, or concrete drum). Due to this second containment and due to the fact that shortly after filling radioactive aerosols are no longer emitted from the product capping of the metal sheet drum has been abandoned.

Air contamination level in the filling chamber was found to be 10 times MPC for α and 50 times MPC for β when processing an evaporator concentrate of 90 Ci/m^3.

An overall decontamination factor of roughly 6000 was found for the distillate from the extruder when processing the above mentioned 90 Ci/m^3 concentrate. This DF holds also for the individual nuclides as Cs-137, Ru-106, Ce-144 and Sb-125, demonstrating a rather good decontamination during normal operation. No further measurable decontamination of the condensates takes place in the oil filter. During plant operation the activity increases, however, in the filter medium by cumulation.

2.3 Off-design conditions

Occasionally the bitumen product discharge became clogged due to material build-up in cavities of the discharge compartment. If the extruder is not shut down in time back pressure forces the product up into the last steam dome, where the continuously produced steam can foam it and force it up as far as the condensers. In such cases the steam dome and discharge compartment have to be dismantled for cleaning. Although these buildups seem to be related to off-standard feed ratios entire clarification has not been obtained. Clogging can however be avoided by inspection of the product outflow and it is completely excluded by a constructional change of the discharge part into forced discharge utilising the transporting action of the extruder.

After roughly 7.500 hours of operation the screws were withdrawn and replaced. An abrasion of up to 7 mm was observed at some of the transporting - and mixing - and kneading disks. Obviously this phenomenon is mainly due to erosive wear which is the more pronounced the higher the salt content of the product. Especially at off-standard feed ratios leading to bitumen depleted products the lubrificating action of the bitumen is drastically decreased. Corrosion can be excluded under normal operation conditions; when, however, processing evaporator concentrates that exceptionally have a too low or too high PH corrosion might play a role, too. Actually tests are performed by the manufacturer Werner & Pfleiderer, with different screws aiming at the determination of a construction material with higher resistance to erosion.

In the course of 4 years of operation, two incidents occurred in the filling chamber. In both cases the bitumen product was foaming and fumes were detected that suddenly caught fire. As a result of this the drums that had received fractions of the corresponding bitumen product caught fire, too (1 drum in the first, 2 drums in the second case). The other drums (5 and 4 respectively) did not burn. Both fires were under control within a short time and could be extinguished with CO_2. No radioactivity escaped from the plant, no person was injured and only little damage and contamination occurred in the filling chamber. In the first incident the fire was caused by ignition of the vapors of organic solvents contained in the waste concentrate. In the other incident, an evaporator concentrate was processed having a pH of 13.8 instead of the standard value 8 to 10. At the same time, the agitator of the concentrate feed tank had failed and a separation of organic compounds contained in the waste (TBP, degradation products, antifoaming agents polyethyleneoxide adducts) could take place. As demonstrated in experiments with the bench scale unit these products are decomposed into easily flammable volatile compounds during incorporation at high alkalinity. The resulting bitumen products had ignition points around 200°C, whereas at pH 8 to 10 no degradation occurs and ignition points of the product are in the region of 400°C. After appropriate pH adjustment with H_3PO_4 the remaining evaporator concentrate was incorporated without any difficulty.

Finally a reaction took place in one bitumen drum in the interim storage bunker. Investigations showed that this drum received a slightly foaming bitumen product that was processed from the final fraction of a non agitated evaporator concentrate in the feed tank containing large amounts of PVC-powder, that - as turned out later - is a filler in pickling pastes used for decontamination and that floats on the surface of evaporator concentrate. This drum-being the last prior to weekend shut down of the plant - was in contrast to the operation instructions not allowed to cool down during 24 hours but immediately after filling with the 200°C bitumen product inserted into a 200 l reinforced drum. This assembly acted as a thermostate and the PVC continued to decompose yielding HCl that most probably initiated an oxidation of the organic material by decomposing nitrates. Although the escaping fumes set an alarm no fire occurred. 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. It's worthwhile mentioning that due to this event a new pickling paste with an inorganic filler was developed that is now exclusively being used at Karlsruhe.

2.4 Process optimisation

Due to the fact that the incidents mentioned in section 2.3 were all in relation with inhomogeneities in the evaporator concentrates measures have been taken for plant shut down whenever the agitator of the concentrate feed tank fails. PH control and adjustment to the mentioned range 8 to 10 is mandatory for operating the bituminization plant. In addition to this DTA analysis of the dry residue of the evaporator concentrate and a 1:1 mixture with bitumen is an excellent indication for eventual off standard samples asking for special treatment.

The electrical installation of the filling chamber is now explosion-proof. The venting system guarantees a fiftyfold air renewal in the filling chamber per hour. Temperature gauges are installed that register any abnormal rise in temperature. Furthermore fume and gas detectors are installed (CO and CH_4 calibrated) that indicate any flammable gas composition in the filling chamber atmosphere. The latter are linked with an automatic fire-extinguishing equipment containing 1.5 t CO_2.

The outlet part of the screw extruder has been modified to avoid clogging of the discharge compartment. In addition inspection of the product discharge is maintained.

Modification of the oil filter for use of filter cartridges that are rejected after saturation instead of reusing the filter housing, leads to an increase in service life of the filter media. The use of filter cartridges substantially reduces the time involved for the filter change, thus allowing higher specific activities on the filters.

Measures are taken for efficient separation of organic solvents from the low and intermediate level effluent streams prior to evaporation (in the vapor compression evaporator).

Operation temperature in the screw extruder is usually limited to 180°C and does never exceed 200°C.

Filled drums are allowed to cool for further 24 hours bringing the centerline temperature of the drums down to the softening point of the product (~100°C). After this cooling period the drums are transported to the interim storage bunker.

Prior to start up and after shut-down of the bituminization of evaporator concentrates the extruder is operated only with bitumen for a period of roughly 15 minutes.

With these measures the bitumen plant has continued extremely reliable operation.

3. RESEARCH AND DEVELOPMENT

As already indicated both the conception of the 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 standard grade Mexphalt 15 or Ebano 15 medium-hard distilled bitumen of 67°C to 72°C ring and ball softening point and a penetration of 10 to 20. Within the existing standard grades this type of bitumen has the highest flash point (> 290°C), another important reason for its selection.

Due to the fact that approximately 30% of the low-level effluents ($\sim 10^{-2}$Ci/m^3) and more than 80% of the intermediate level effluents ($\leq$ 100 Ci/m^3) result from the reprocessing plant, they contain rather high $NaNO_3$ concentrations. In fact the $NaNO_3$ content in the salt residues of the evaporator concentrates actually processed amounts to up till 70wt%. This is why the largest part of the investigations were strictly devoted to the safety aspects related to both the processing of such high nitrate containing evaporator concentrates and to the resulting products. The problem of bitumen oxidation and hardening was thus thoroughly investigated {4}. It could be concluded that hardening and oxidation of the bitumen can safely be avoided by incorporating at slightly alkaline conditions, at temperatures $\leq$ 200°C and preferrably at short residenc times. The latter two conditions are best met in a screw extruder.

3.1 Thermal stability

One of the safety aspects that has received considerable attention was the thermal stability of the products. An exhaustive investigation was performed at the Institute for the Chemistry of Propellants and Explosives (ICT) on the thermal and mechanical sensitivity of bitumen/oxygen salt mixtures {5}. Investigations were performed mainly with bitumen products of 60 wt.% nitrates from various metals and other additives that were expected to be potential constituents of evaporator concentrates. The high salt content compared with that of the actual products prepared in the plant (~50 wt%) has purposely been selected to be on the safe side. Bitumen products and pure bitumen showed the same behaviour on 40 hours heating at 100°C under vacuum, demonstrating good compatibility of the salt mixtures with bitumen. Ignition temperatures of the products were above 400°C, only some samples with increased fractions of calcium-nitrate and transition metal nitrates showed ignition temperatures between 360° and 380°C. Combustion behaviour studied in the red hot steel pan (~700°C) showed a faster time to ignition for the bitumen products (1 to 5 sec) than for the pure bitumen (30 sec); the burning periods were of the same order of magnitude, with the bitumen products burning more briskly than the pure bitumen. Rapid heating under contained conditions demonstrated that there was no hazard of explosion. Furthermore the products were not sensitive to mechanical stresses and detonation stresses. The investigations thus demonstrated, that the products investigated do not belong to the category of substances involving an explosion hazard.

In addition 175 l sheet-metal drums containing 57:43 wt% bitumen: $NaNO_3$ products were ignited by powerful oilfires in field tests to study the combustion behaviour and fire fighting measures {6,7}. The tests confirmed, that the products cannot be considered easily flammable. During the first 10 minutes the combustion was peaceful, afterwards partially vigorous (obviously due to the decomposition of $NaNO_3$) but never leading to a deflagration or explosion. Total combustion time for 211 kg bitumen product (87% filling of the 175 l drum) was 85 minutes, roughly 27% of the $NaNO_3$ was carried with the fumes most probably as Na_2O aerosols. Fire fighting tests have demonstrated that bitumen product fires can be brought under control without difficulties and that CO_2 is the most suitable fire extinguishing medium (see sections 2.3 and 2.4). Combustion tests will be completed by exposing bitumen product packages (175 l sheet metal drum in a 200 l reinforced drum or a prepfabricated concrete container, see section 2.2) to oil fires.

The question whether bitumen products might catch fire as a consequence of an eventual ignition of an hydrogen - air mixture resulting from radiolysis (see section 3.3) is actually under investigation at the ICT. First tests in a simulated small scale storage chamber demonstrated that ignition of various H_2/air mixtures with H_2 contents between 4.3 and 10.5 vol.% did not lead to an inflammation of the bitumen product test-specimen. Although these tests demonstrate again that the bitumen products are not easily flammable, full scale gas explosion tests with a couple of 175 l sheet-metal drums containing bitumen products will be performed this year in a special blasting bunker.

Differential thermal analysis (DTA) is an excellent tool for the determination of the thermal stability of chemical compounds. DTA curves of active bitumen product samples from the plant show all endothermic peaks in the temperature range between 270°C and 300°C. Exothermic peaks are generally observed in the region of 400°C. It could be shown that the endothermic peaks indicate the melting point of $NaNO_3$ (306°C) which due to other salt impurities can considerably be lowered {8}. The exothermic peaks around 400°C coincide generally with the burning points of the mixtures, as determined by a non standardized test procedure where 1 g of product is heated on a steel plate in presence of a fanning flame. Endothermic peaks in the region of the operation temperatures of the extruder generally indicate volatile organic compounds. The antifoaming agents, for instance, that were originally utilised in the vapor compression evaporator showed marked endothermic peaks at 130°C and have been replaced by a more stable compound. Due to the significant information on the thermal behaviour DTA tests are routinely performed both in plant operation and R+D-activities.

The above mentioned test procedure, although not standardized, has proven to be a very reliable method since starting investigations on thermal stability. Testing various bitumen grades, lowest burning points (260° to 300°C) were found for Mexphalt R85/40 or R 90/40 blown bitumen and highest burning points (410°C to 440°) were found for standard grade bitumen Mexphalt 15 or Ebano 15. Various nitrate salt mixtures with the latter bitumen grades showed burning points well above 300°C, generally in the region of ≥ 400°C {9}, being in excellent consistency with the values measured by ICT {5}. Burning points of 50 wt.% bitumen products obtained in the bench scale unit from simulated power reactor wastes (spent mixed bed ion exchanger, evaporator concentrates with high boric acid - or high tenside content) showed values well above 400°C {10}.

In connection with the reconnaissance of the incident mentioned in section 2.3 a simulated evaporator concentrate solution containing 175 g/l $NaNO_3$, 5 g/l $NaNO_2$ and 20 g/l of a 1:1 mixture of dibutyle- and monobutyle phosphoric acid was incorporated at pH 11 and pH 13.5 in the bench scale unit yielding 50 wt.% bitumen products. Operation temperatures were as in the production plant. In contrast to the product of low alkalinity, the product of high alkalinity was vigorously foaming. The burning point of the product was at 200°C whereas the product of low alkalinity had a burning point of 400°C. In contrast to this result the burning point of the product was not lowered when incorporating an evaporator concentrate with only 1.5 g/l DBP/MBP at high pH. This and similar experiments demonstrated that at high alkalinity organic compounds can be decomposed into easily flammable compounds at the operation temperatures of the extruder. Care has thus to be taken for a homogeneous feed and a pH adjustment between 8 and 10.

3.2 Resistance to leaching

Apart from thermal stability resistance to leaching is another important property needed for the characterization of solidified radioactive wastes. Leach tests were performed with numerous bitumen products containing roughly 40 wt.% salts of representative composition for the evaporator concentrates of the Research Center {4,11}. Leaching was measured in distilled water for one year by determining the amount of sodium leached. The average leach rate of 16 different products was $5 \cdot 10^{-4} \cdot g \cdot cm^{-2} \cdot d^{-1}$ with $1 \cdot 10^{-5}\ g \cdot cm^{-2} \cdot d^{-1}$ being the lowest and $2 \cdot 10^{-3} g \cdot cm^{-2} \cdot d^{-1}$ the highest value. The simultaneous determination of sodium, iron and calcium did not reveal any significant differences in the specific leach rates of these ions.

A direct proportionality of the leach rate with the amount of salt incorporated was found for bitumen-$NaNO_3$ products as indicated in table I.

Table I Leach rates of bitumen / $NaNO_3$ products as a function of $NaNO_3$ concentration (average values over 1 year)

$NaNO_3$ content {wt.%}	0.1	1	5	10	20	38.5
leach rate { $g \cdot cm^{-2} \cdot d^{-1}$ }	not detectable	not detectable	$4 \cdot 10^{-6}$	$7 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$9 \cdot 10^{-5}$

Another interesting result is the relation between the leach rate and the dispersion of the salts in the bitumen products. In experiments with bitumen products containing 38.5 wt.% NaCl of defined particle size it was demonstrated that products with coarser crystals are more easily leached than products with finer crystals. After one year the product samples with crystals of the sieve fraction 0.5 - 0.8 mm showed a cumulative leaching between 0.7 and 1% compared with the 0.1% value of the product samples with crystals of the sieve fraction 0.05 - 0.08 mm. 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.

Products of bad leach resistance have been found when incorporating sodium carbonate into bitumen. A product containing for instance, roughly 19 wt.% $NaNO_3$ and 19 wt.% Na_2CO_3 had an average leach rate (1 year) of $2 \cdot 10^{-3}$ g $\cdot$ $cm^{-2} \cdot d^{-1}$. For a bitumen product containing 38,5 wt.% Na_2CO_3 an average leach rate of $1 \cdot 10^{-2}$ g $\cdot$ $cm^{-2} \cdot d^{-1}$ was measured during 84 days. At the same time these products showed considerable swelling when stored under water. The 38.5 wt.% Na_2CO_3 sample had after 14 days immersion approximately doubled its original volume. This anomalous behaviour was also noticed in the shape of the leaching curve that, in contrast to normal findings showed after 3 days immersion in water a sharp linear increase of the differential leach rate during a period of one week.

Similar exceptional leaching behaviour was found for bitumen products containing Na_2SO_4. As for the Na_2CO_3 samples an increase in the differential leach rate was observed. Cumulative leaching during 7 days from ~ 10 cm Ø and ~ 7 cm high samples amounted to 49.2%, 10.9% and 1.2% for bitumen products containing 50 wt.% 39 wt.% and 30 wt.% Na_2SO_4. The products suffered from swelling, too, as indicated by pointed cone-shaped elevations forming after 7 days immersion in water. As in the case of the Na_2CO_3 samples, this behaviour is most probably due to the fact that both Na_2CO_3 and Na_2SO_4 in their anhydrous form tend to bind considerable amounts of water of crystallization. This reaction leads in turn to a pronounced increase in the volume of the crystals, that provokes crevices in the bitumen product thus enlarging the entrance of further water into the bitumen matrix.

During an experimental program performed with the bench scale unit to define operation conditions for the bituminization of power reactor wastes, some products were found that did not completely correspond with the good leaching characteristics of bitumen products normally encountered {10}. A bitumen product containing 53 wt.% bitumen and 47 wt.% salt residues of an evaporator concentrate composed among other constituents mainly of boric acid (150 g/l H_3BO_3) alkalized by 82 g/l NaOH to pH 12, showed an average leach rate over 100 days of $7 \cdot 10^{-3}$ g $\cdot$ $cm^{-2} \cdot d^{-1}$. Another bitumen product containing 50 wt.% salt residue, more than 2/3 of which were detergents, soap powder and laundry cleansing agents revealed an average leach rate of $1.5 \cdot 10^{-2}$ g $\cdot$ $cm^{-2} \cdot d^{-1}$ during 100 days leaching. The products showed some swelling upon immersion in water, too. This behaviour is due to the high alkalinity and the large amounts of detergents that have an emulsifying and dispersing action.

An amelioration of the resistance to leaching can be obtained either by chemical pretreatment of the concentrates prior to incorporation or by coating the final products with a layer of pure bitumen. A 38.5 wt.% $NaNO_3$ containing bitumen product covered with a 5 mm thick coating of pure bitumen had for instance an average leach rate of $3 \cdot 10^{-8} \cdot$ g $\cdot$ $cm^{-2} \cdot d^{-1}$ after 5 years continuous leaching i.e. a leach rate that is almost 4 orders of magnitude lower than that of the uncoated product. A 40 wt.% Na_2SO_4 containing bitumen product with a similar coating did not swell at all when immersed in water. The same was true for a bitumen product containing 17 wt.% Na_2SO_4, 17 wt.% $CaSO_4$ and 14 wt.% NaCl, i.e. a product that has been obtained by incorporating a Na_2SO_4 solution where half of the Na_2SO_4 had previously been precipitated by $CaCl_2$. Leach tests are still continuing, indicating drastically reduced leach rates. These examples demonstrate, that products of adequate leaching behaviour can successfully be obtained by appropriate chemical pretreatment and/or coating.

3.3 Stability towards radiation

For the performance of external radiation tests two radiation sources have been utilized: A linear accelerator for 10 MeV electron pulses (frequency 170 sec^{-1}, time 5 μsec) with an "apparent" dose rate of roughly $8 \cdot 10^6$ rad/h and an irradiation facility in a fuel element storage pond with an average γ dose rate of 10^5 R/h.

First irradiation tests with various bitumen types and different bitumen/salt mixtures (61.5/38.5 wt.%) indicated that a marked increase in the softening point and thus a change in the viscoelastic properties of bitumen and bitumen/salt mixtures can first be noticed at irradiation to $\geq$ 100 Mrad {4}

Irradiation tests with distilled bitumen (Mexphalt 15) blown bitumen (Mexphalt R 90/40) and their corresponding products containing 50 wt.% $NaNO_3$, were performed with 10 MeV electrons from the linear accelerator {12}. When irradiated to $5 \cdot 10^8$rad the blown bitumen and its corresponding product showed a very pronounced <u>increase in the softening point</u> (90°C to 117°C and 113°C to 159°C, respectively). When heating the blown bitumen during 5 hours to 150°C prior to irradiation this increase was still more pronounced (117°C to 155°C). For the distilled bitumen and its corresponding product a rather small increase was found (77°C to 83°C and 101°C to 108°C). All pure bitumen samples and their corresponding products showed <u>marked swelling</u> after irradiation to $5 \cdot 10^8$rad: Porosities ($\varepsilon = 1 - \frac{\varrho'}{\varrho}$) (1) after irradiation were between 0.1 (Mex 15) and 0.4 (Mex. R90/40) and around 0.3 for the two corresponding products. <u>Hydrogen production</u> at an irradiation to $1 \cdot 10^8$ rad was 0.71 cm^3/g (Mex. R90/40) and 0.56 cm^3/g (Mex 15) for the pure bitumen samples whereas roughly half these values were found for the corresponding products 0.33 cm^3/g and 0.24 cm^3/g. It is interesting to note that a 5 hours heat treatment at 150°C prior to irradiation lowers the hydrogen production of the bitumen by about 10%.

A bitumen product containing 57.2 wt.% Ebano 15, 42 wt.% $NaNO_3$, 0.75 wt.% H_2O and 0.05 wt.% NaOH, that was produced during the cold start up of the bitumen plant showed porosities of 0.006, 0.14, 0.22 and 0.26 after irradiation with 10 MeV electrons to total absorbed doses of 10^7, $5 \cdot 10^7$, 10^8 and $5 \cdot 10^8$ rad respectively {6}. For both irradiation with 10 MeV electrons and γ radiation from the fuel element storage pond a linear relation was found between the amount of H_2 formed and the absorbed dose within the 100 Mrad dose range investigated. The specific hydrogen production rate determined was between 0.4 and 0.5 cm^3/g and 100 Mrad {7}. Though in the same order of magnitude as the values cited above this value is somewhat higher. As the hydrogen production has a certain influence on the storage conditions (H_2 accumulation in the atmosphere) further tests will be performed by studying the radiation stability with internal radiation from incorporated radionuclides in cooperation with EUROCHEMIC.

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(1) ϱ': density after irradiation, ϱ : density without irradiation

Irradiation of the bitumen products produced from spent power reactor ion exchange resins and simulated evaporator concentrates rich in borates and detergents (see sections 3.1 and 3.2) {10}showed porosities between 0.01 and 0.04 for irradiation with both 10 MeV electrons and γ radiation to a total integrated dose of 80 Mrad. Hydrogen production was 0.3 cm^3/g for 80 Mrad.

As already mentioned the investigations of the radiation stability will be terminated in cooperation with EUROCHEMIC by internal irradiation tests utilising representative bitumen products with incorporated fission products and α-emitting transuranium elements.

4. CONCLUSION

In concluding it can be stated 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 wastes. The screw-extruder technique proved to be very reliable and flexible for continuous incorporation to extremely homogeneous products.

Escorting R+D work by operating a bench-scale unit of exactly the same features as the plant and by characterizing the products obtained for their thermal stability, leachability and radiation stability has proven to be a very valuable supplement both with respect to plant operation and to the definition of incorporation conditions for new types of radwaste.

From a radiation resistance point of view bituminization has, however, to be limited to integrated total doses of 10^8 to 10^9 rads, a dose range corresponding to the category of medium level wastes. In this connection, and due to the experience gained, there is no doubt that bituminization is very well suited for the solidification of waste concentrates from power reactors and will thus find a broad application in the future. As far as medium level waste streams from reprocessing plants are concerned work is continuing to still further increase the safety of this process by applying processes that reduce both the activity and the nitrate content from these wastes {13}.

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