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PYROCHEMICAL HEAD END CONCEPTION FOR FAST BREEDER FUEL PROCESSING

by

J.G. WURM (Euratom), P.R. HEYLEN (CEN)
R.C. DE BEUKELAER and A. DE CONINCK
(BelgoNucléaire)

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BelgoNucléaire S.A., Brussels - Belgium
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CEN - Centre d'Etude de l'Energie Nucléaire, Mol - Belgium
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Reaktortagung 1970
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ABSTRACT

The work presented in this report concerns an integrated pyrochemical head end based on the decladding of the stainless steel canning in a liquid solvent alloy composed of Sb-Cu and followed by a disaggregation of the fuel in a molten oxidizing salt bath composed of alkaline nitrates. Two different Sb-Cu dissolution procedures are described and a materials abalance is given as well for the liquid metal dissolution as for the molten salt disaggregation.

KEYWORDS

SOLVENT EXTRACTION
DECLADDING
ANTIMONY ALLOYS
COPPER ALLOYS
STAINLESS STEELS
FUSED SALTS
DECOMPOSITION

C O N T E N T S

PYROCHEMICAL HEAD END CONCEPTION FOR FAST BREEDER FUEL PROCESSING *)

I. General considerations

The aqueous processing of L.W.R. fuels has now reached industrial maturity. The fundamental aspects are well understood and only optimization problems of the existing aqueous processing plants are still to be solved. However, with the event of the highly irradiated fast breeder fuels new difficulties will have to be overcome.

A few years ago the opinion prevailed that only dry processing methods such as the halide volatility or pyrochemical methods would be able to process fast breeder fuels. This situation has changed recently since it is well accepted now that the aqueous reprocessing methods are also feasible for fast reactor fuels. The difficulties however are located mainly in the head end step, particularly if short cooled fuels are considered. This opinion was also clearly expressed by the I.A.E.A. Panel on Highly Irradiated Fuels at Vienna in May 1969. /1/.

The problems arising with highly irradiated short cooled fast breeder fuels are as follows :

- the presence of Na either attached or locked inside the fuel pins ;
- the high Pu content affecting the chemistry and creating criticality problems ;

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- the high concentration of fission products ;
- the release and conditioning of large amounts of gaseous fission products, particularly I_2, H_3, Xe and Kr ;
- solvent degradation problems ;
- heat release in the fuel.

Most of these problems must be faced in the head end steps, which include such operations as receiving, unloading, storage, decanning, fuel preparation for the dissolver and off gas treatment. Different head end approaches are under investigation in various countries.

Watson et al. from ORNL [2] described a head end processing step based on a more classical shearing device of dismantled fuel pins followed by a dry oxidization step and acid leaching.

G.P. Novoselov et al. from the USSR [3] described a thermal decladding method based on a melting procedure of the stainless steel cladding.

W.G. Walsh and R.D. Pierce from ANL [4] described a decladding method by which the stainless steel cladding is dissolved in molten zinc.

The work presented in this paper concerns an integrated pyrochemical head end based on the decladding of the stainless steel canning in a liquid solvent alloy composed of Sb-Cu, and followed by disaggregation of the fuel in a molten oxidizing salt bath (alkaline nitrates). The fundamental aspects of the liquid metal decanning and the molten salt disaggregation have been worked out at Euratom, Ispra [5] [6]. The results are given in the I.A.E.A. report No. 115, Vienna, May 1969.

Conceptual design studies and scaling-up of this process are now performed at S.C.K./C.E.N., Mol in connection with S.A. Belgonucleaire and the CCR Euratom, Ispra.

II. Fundamental aspects

Optimum dissolution performance of the stainless steel and other high nickel alloys could be obtained with an Sb-Cu (10-23.5 wt.%) solvent alloy at 900-1000 °C as seen in Fig. 1, 2 and 3. Na solubility measurements have shown that at least 0.8 wt.% of Na could be retained in the Sb-Cu alloy at 900 °C at normal pressure. Structural materials such as high density graphite, W, WC and Al_2O_3 and ZrO_2 are compatible with the dissolution process. No side reactions of PuO_2 with the solvent alloy could be detected. Separation of the fuel and the solvent alloy was performed on porous graphite filters without difficulties.

Furthermore, it has been established that UO_2-PuO_2 (20 wt.%) fuel can be oxidized and completely disaggregated into a fine powder by means of molten nitrates at 600 °C (only 450 °C for UO_2). In this molten salt oxidization step the UO_2 is completely transformed into sodium uranate U_2O_7Na while the Pu remains as PuO_2. Since the solid solution crystal lattice is destroyed, all the gaseous fission products are released and can be collected in a condensed form.

III. Technological aspects

On hand of these positive laboratory results an attempt was made to integrate all the different unit steps into a fully integrated head end flow sheet suitable for an aqueous

processing plant. This head end flow sheet illustrated by Fig. 4 covers all the necessary operations from the fuel reception line to the feed preparation for the acid leacher and is divided into the four following steps :

- receiving and storage of the irradiated fuel elements;
- liquid metal dissolution and fuel filtration ;
- fuel disaggregation by molten salts or oxidization in a fluid bed ;
- gaseous and solid waste treatment and conditioning.

III.1. Receiving and storage

Up to now it is not clear whether the shipping cask will be Na or gas cooled. Also the chosen cooling procedure (Na or gas) would not interfere with the subsequent head end which is proposed. However, for reasons of thermal efficiency and design simplicity, shipping and storage under Na would be the preferred solution, since the presence of Na either attached or locked inside the fuel pins would be "compatible" with the liquid metal decanning procedure.

III.2. Canning dissolution and fuel filtration

The liquid metal dissolution can be performed in an adequately designed furnace in two different ways, as illustrated by Fig. 5 :

- complete dissolution of the pins and the hexagonal wrapper through progressive or total immersion under agitation of the fuel element in the solvent alloy;
- selective dissolution of the fuel pins only, leaving the main part of the hexagonal wrapper undissolved.

In the first case the dissolution furnace is filled with the Sb-Cu quantity necessary to dissolve completely 3/4 of the fuel element from the bottom to the fission gas cavities. The heating system is provided only in the lower part of the furnace. A mechanical rotating device for the fuel element and fission gas evacuation line are foreseen at the furnace top. At the start the furnace is flushed with an inert gas.

In the second case, the furnace design is similar ; however, the heating system covers the whole length of the furnace. The mechanical rotating device is replaced by a hydraulic pulsating system of the solvent alloy inside the wrapper in order to reach a quick and selective dissolution of the fuel pins. Due to the wall thickness difference between the pins (0.38 mm) and the wrapper (2.5 - 3 mm) the latter remains practically undissolved. The fission gas evacuation line is connected directly to the fuel element. Consequently the dissolution time will be reduced as well as the consumption of the solvent alloy.

III.3. Fuel separation

After the cladding dissolution the UO_2-PuO_2 fuel remains in suspension in the solvent alloy + stainless steel since the density difference between both is very small. This fuel suspension is then transferred to the fuel filtration unit by which the fuel is filtered on porous graphite. At the output of the filter unit the solvent alloy + stainless steel flows directly into a waste storage container ready for permanent conditioning. The fission gas lines of the filtration unit and the furnace are joined together and both streams are condensed and conditioned. Finally the filtered fuel is transferred to the oxidization and disaggregation unit.

III.4. Fuel oxidization

The main purpose of the oxidization step consists in preparing the fuel for the acid leacher and particularly to separate such gaseous fission products as iodine and tritium which are undesirable during aqueous processing. Therefore the UO_2-PuO_2 solid solution crystal lattice must be completely destroyed. Two different ways are foreseen :

- oxidization of the UO_2-PuO_2 by air or O_2 in a fluid or fixed bed at about 1000 °C ;
- oxidization and disaggregation of the fuel by means of a molten oxidizing salt (alkaline nitrates).

Hot cell laboratory experiments, on small highly irradiated UO_2-PuO_2 fuel samples, are scheduled at Mol in the near future. On hand of these experiments it will be possible to decide for the most adequate oxidization step. However, cold laboratory oxidization experiments on non-irradiated synthetic UO_2-PuO_2 (18 wt.%) fuel gains (Ø 3 mm) performed at 950 °C in a O_2 stream have already shown that the fuel grains are not pulverized even if a fractional weight increase takes place (thermobalance experiments).

With molten oxidizing salts on the contrary, a complete disaggregation of a UO_2-PuO_2 (20 wt.%) is already reached at 600 °C. If the hot cell oxidization experiments behave similarly, the molten salt technique might be the best choice.

The pulverized fuel will be separated from the molten salts by filtration and transferred immediately to the acid dissolver. The molten salts are then recycled and regenerated with Na_2O_2 for another series of oxidization until they are saturated with fission products. Another plus point for the molten

salts is the slight decontamination factor which results from this operation. Such F.P. as Cs, Sr, Ba, Mo, Ru are soluble in the molten salts and are discarded in the solid salt waste.

A conceptual design view of the head end hot cell operations is given in Fig. 6.

IV. Material balance

As an example of the pyrochemical head end possibilities, material balances are given in Fig. 7, 8 and 9, based on a Na I core fuel assembly of the 1-3 and 2-4 zone.

Following hypotheses are retained : the dissolution rate of the stainless steel in the solvent alloy would be limited to 35 wt.%. The upper part of the fuel element, which does not contain fuel, representing about 1/3 of the stainless steel weight, (50 kg), will not be dissolved in the solvent alloy. It is further assumed that about 1000 g of Na are carried along with each fuel element (100 g locked inside 1 % of the pins and 900 g attached to the surface).

Fig. 7 and 8 show that about 2 kg Sb-Cu/kg fuel are necessary for complete dissolution and only 1 kg Sb-Cu/kg fuel for selective dissolution. The solid waste volume of the discarded solvent alloy including all the stainless steel (medium density 7.8) is respectively 60 l and 40 l per fuel element.

The quantities involved in the molten salt disaggregation are given in Fig. 9. For this operation, the molten nitrate quantity used at the start, corresponds to the fuel quantity

of three fuel elements, since for a good reaction efficiency an excess volume will be necessary. Therefore, two nitrate regeneration cycles with Na_2O_2 are foreseen before the nitrate bath becomes saturated with F.P. and is discarded to the waste.

For the oxidization reaction of one fuel element (UO_2 135 kg ; PuO_2 18 kg ; F.P. 6.5 kg) a theoretical quantity of 45 kg NO_3Na and 16 kg Na_2O are necessary. After fuel filtration a solid salt waste quantity of 43 kg (NO_3Na 30 kg ; NO_2Na 11 kg ; P.F. 3.3 kg) representing a volume of 17 l is evacuated.

In short : total solid waste volume for one fuel element : solvent alloy + stainless steel + salt waste not including the fission gases represents for :

- complete dissolution : 60 + 17 = 77 l
- selective dissolution : 40 + 17 = 57 l

V. Pyrochemical head end evaluation

A short evaluation of the pyrochemical head end including advantages and disadvantages as well as the technological problems still to be solved is given in Fig. 10.

The main features are as follows :
The pyrochemical head end is almost completely independent of the cooling procedure, which is chosen either for the shipping or storage. Na or gas cooling would have only minor incidences on the process.

The presence of Na is well compatible with the decanning procedure since Na is soluble in the solvent alloy. Consequently a costly Na dislodging device, as it is foreseen

with a mechanical chopping, would not be necessary. No mechanical disassembling device is needed either.

Furthermore, monitoring and control devices for detecting and separating failed fuel elements and special storage and treatment equipment can be left out, since no distinction has to be made between intact and Na locked fuel pins before the liquid metal decanning.

The universal character of the liquid metal decanning is also an appreciable advantage. The system works with almost any known geometry of the fuel element : it does not matter, therefore, whether the fuel element has welded grids or spiral spacers.

Due to the great dissolution flexibility of the Sb-Cu solvent alloy, almost all known fast breeder structural materials such as the various austenitic stainless steel types, the high nickel alloys, the ferritic steels and to some extent Ti, Va and Zr alloys can be dissolved efficiently by changing simply the Sb-Cu ratio of the solvent alloy.

On the negative side, the technological problems concerning the fuel-solvent alloy separation, in order to minimize the PuO_2 losses, must be improved and tested on a large scale facility.

The molten salt step is characterized by a low temperature (600 °C) oxidization for a complete disaggregation of the fuel and the extraction of the fission gases, particularly I_2 and H_3 in the most possible condensed form. Despite the handling of molten salts and its connected waste problem, this technique seems to be more attractive than the straight high temperature (1000 °C) O_2 oxidization using large gas volumes mixed with appreciable amounts of fission gases.

The conditioning and permanent storage of the head end solid waste including the solvent alloy + stainless steel + salt does not involve major difficulties since the total volume to be discarded represents only 77 l per fuel element. This figure corresponds to a waste volume of about 500 l/t of UO_2-PuO_2 fuel.

Additional advantages : the compactness of the equipment, the reduced number of unit operations, the compact solid waste, the safe criticality configuration and finally the easy NO_3H dissolution of the pulverized fuel.

VI. Conclusions

The pyrochemical head end described above presents a series of inherent advantages for the processing of short-cooled fast breeder fuels. It is therefore considered as a valuable alternative to the mechanical head end. However, since the pyrochemical head end relies on a more advanced technology a research and development effort is still necessary to bring it to maturity. In view to compare both methods, technically and economically, further experiments on dummy fuel elements on a representative scale are scheduled and a comparative conceptual head end file will be established to the end of 1970.

VII. Acknowledgement

The authors acknowledge the contribution and participation in discussion of C. David and A. Avogadro from Euratom Ispra. Sincere thanks are due to P. Henrion, W. Claes and co-workers for their work on reaction kinetics.

VIII. References

/1/ IAEA-115, Panel on reprocessing of highly irradiated fuel, Vienna, May 1969, Summary and recommendations, p.383.

/2/ C.D. WATSON et al., ORNL, Head end processing of spent LMFBR fuel, Proceedings of the 16th conference on remote systems technology, 1969.

/3/ G.P. NOVOSELOV et al., USSR, Thermal method of decladding stainless steel canned fuel elements, 36ème congrès international de chimie industrielle, Bruxelles 1967.

/4/ W.J. WALSH and R.D. PIERCE, ANL, Liquid metal decladding processes for fast breeder fuel reprocessing, ANS meeting, San Francisco, November 1969.

/5/ J.G. WURM, M. PAYRISSAT, Liquid metal decanning of highly irradiated UO_2-PuO_2/stainless steel clad fuels, IAEA-115, Panel on reprocessing of highly irradiated fuels, Vienna May 1969, p.167-181.

/6/ A. AVOGADRO and J.G. WURM, Pyrochemical separation and extraction of plutonium in highly irradiated ceramic fuels, IAEA-115, Panel on reprocessing of highly irradiated fuels, Vienna, May 1969, p.149-166.

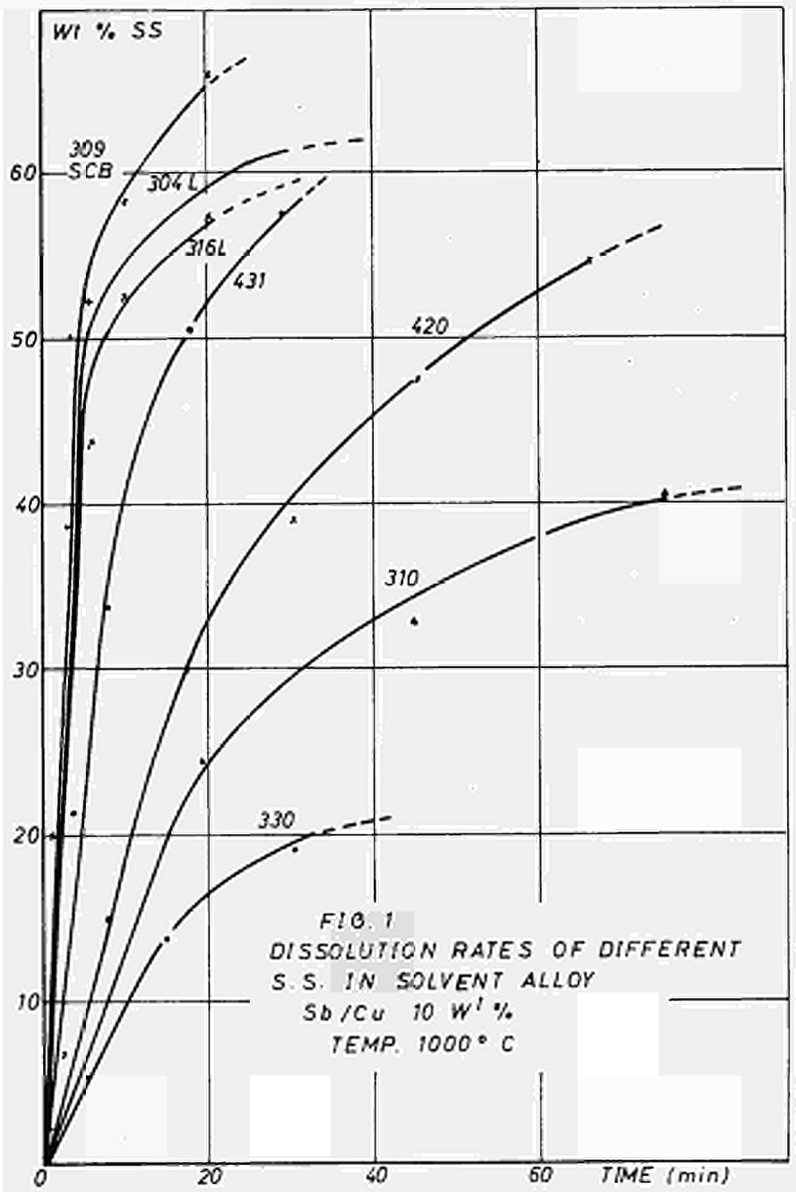


FIG. 1
DISSOLUTION RATES OF DIFFERENT S.S. IN SOLVENT ALLOY
Sb/Cu 10 W¹ %
TEMP. 1000° C

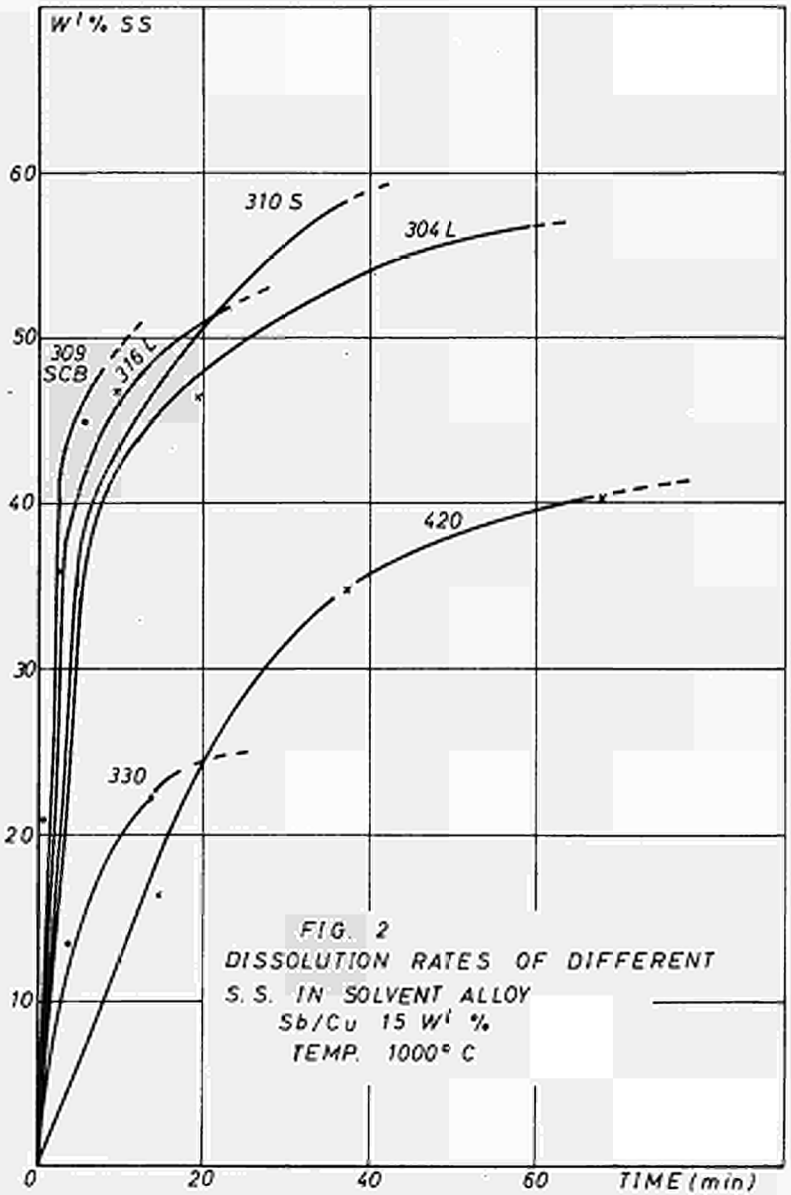


FIG. 2
DISSOLUTION RATES OF DIFFERENT S.S. IN SOLVENT ALLOY
Sb/Cu 15 W¹ %
TEMP. 1000° C

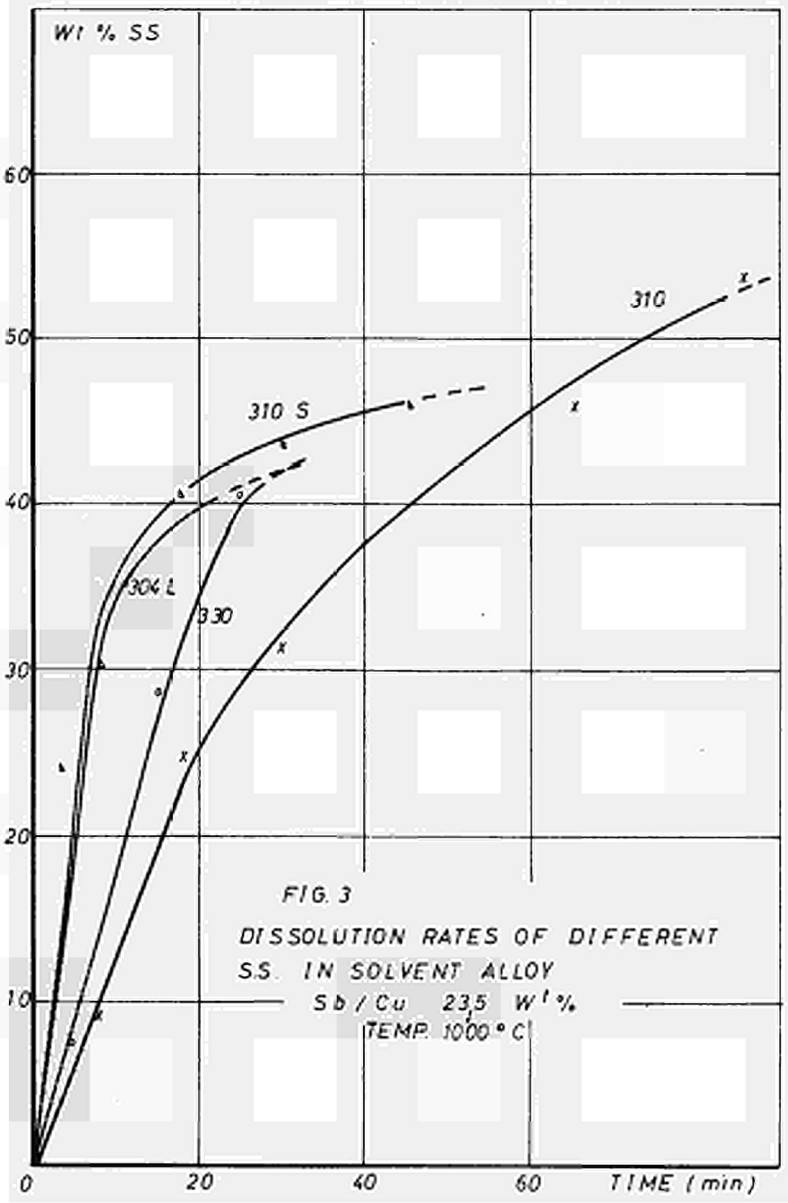


FIG. 3

DISSOLUTION RATES OF DIFFERENT S.S. IN SOLVENT ALLOY

Sb / Cu 23,5 W t %

TEMP. 1000 °C

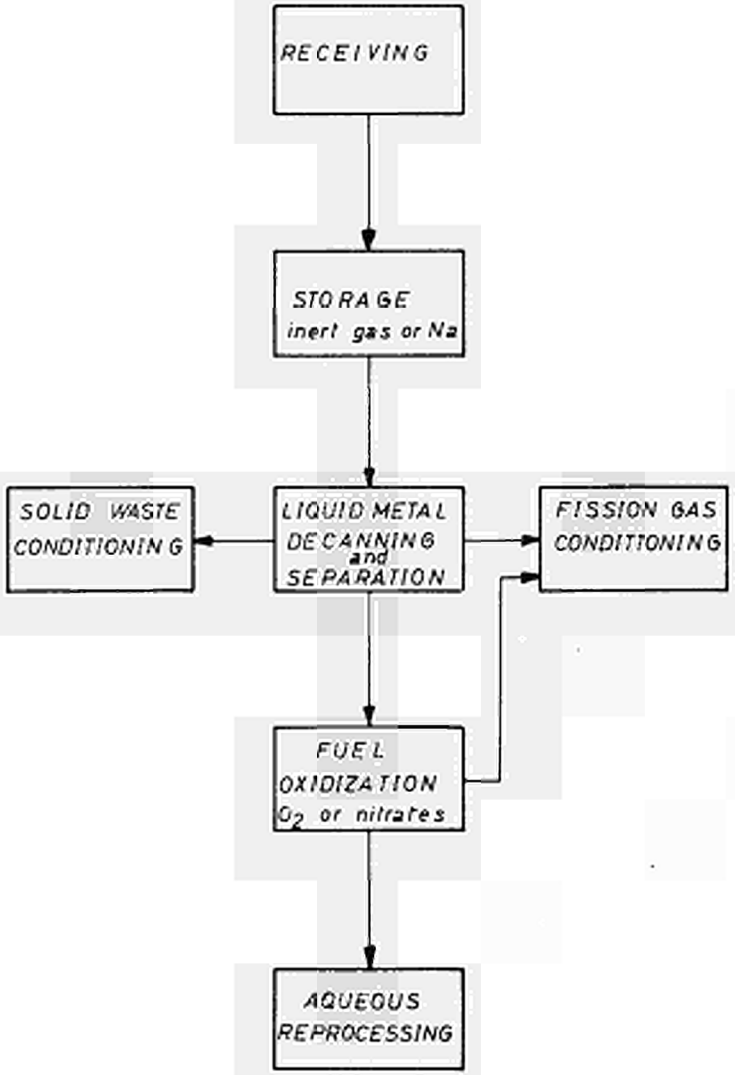


FIG. 4

INTEGRATED HEAD END FLOW SHEET

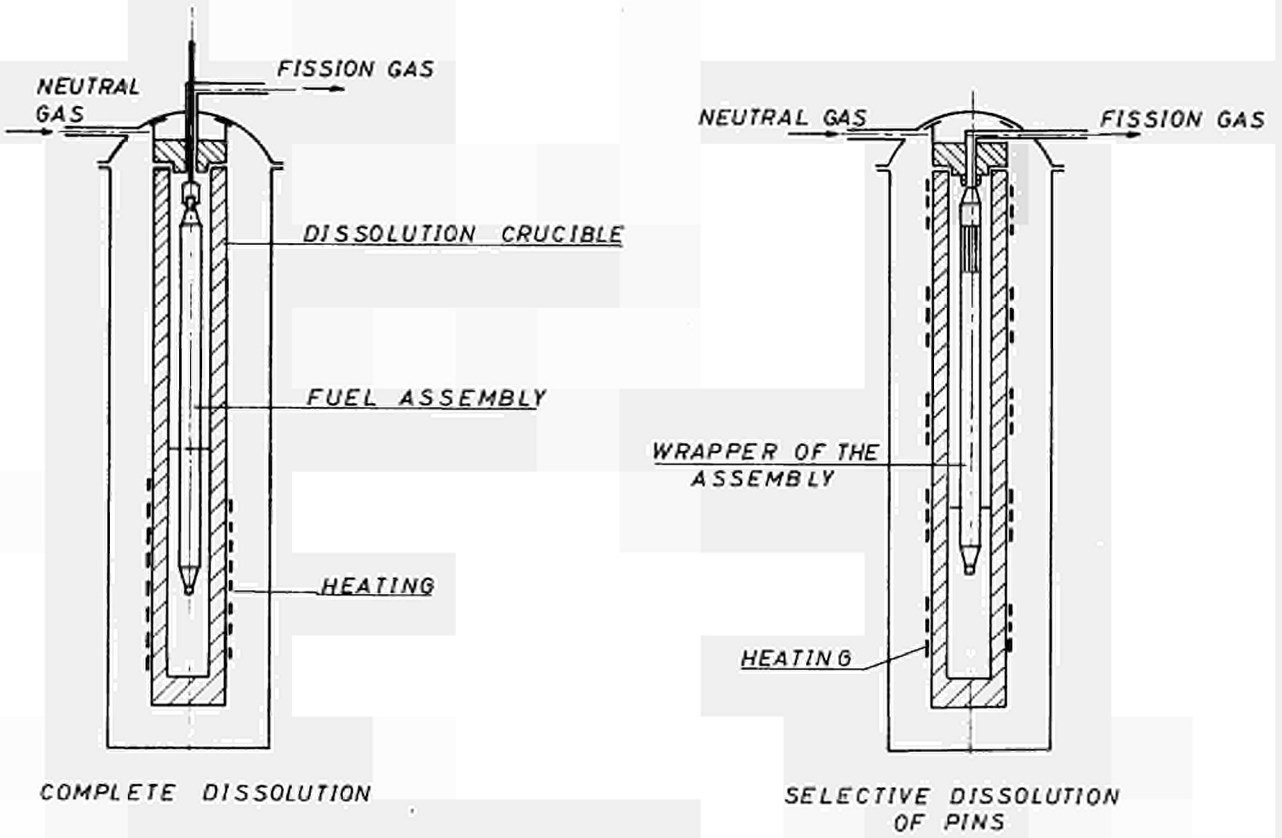


FIG. 5 DISSOLUTION SYSTEMS

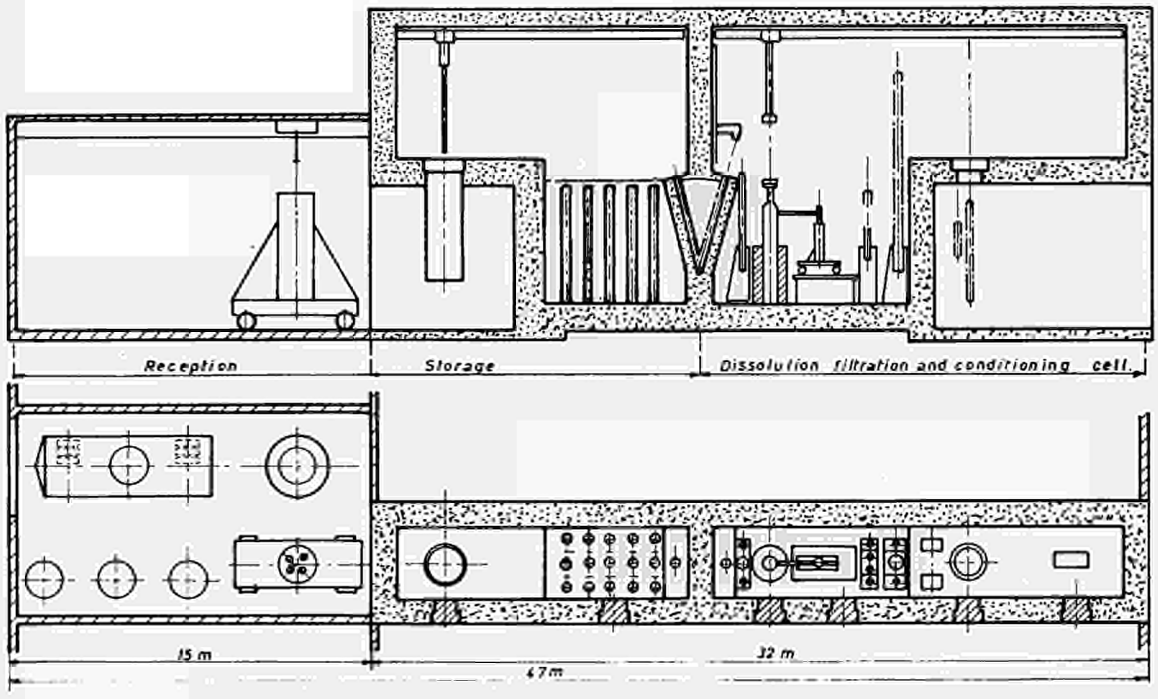


FIG. 6 HEAD END CONCEPTUAL DESIGN OF THE HOT CELL

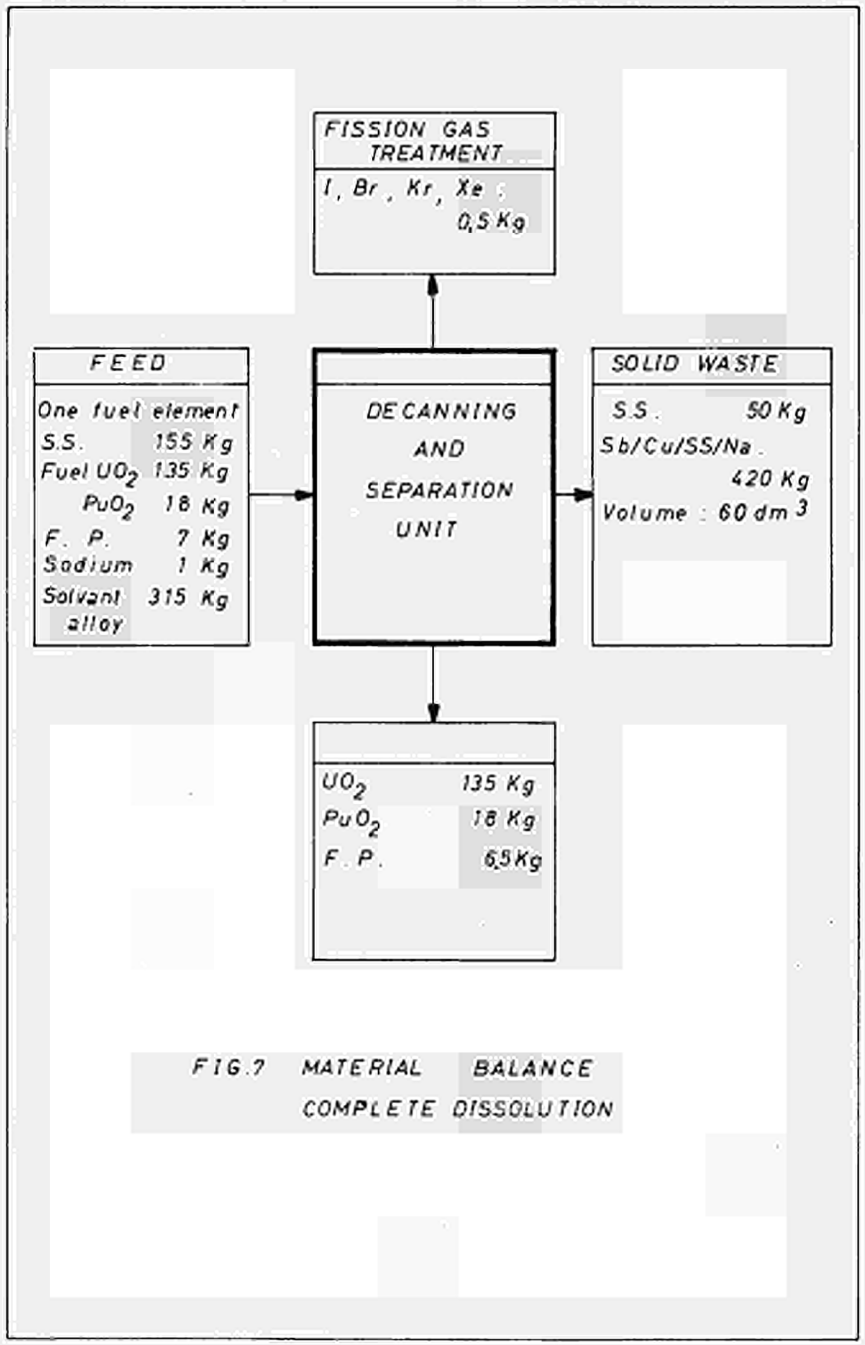


FIG.7 MATERIAL BALANCE
COMPLETE DISSOLUTION

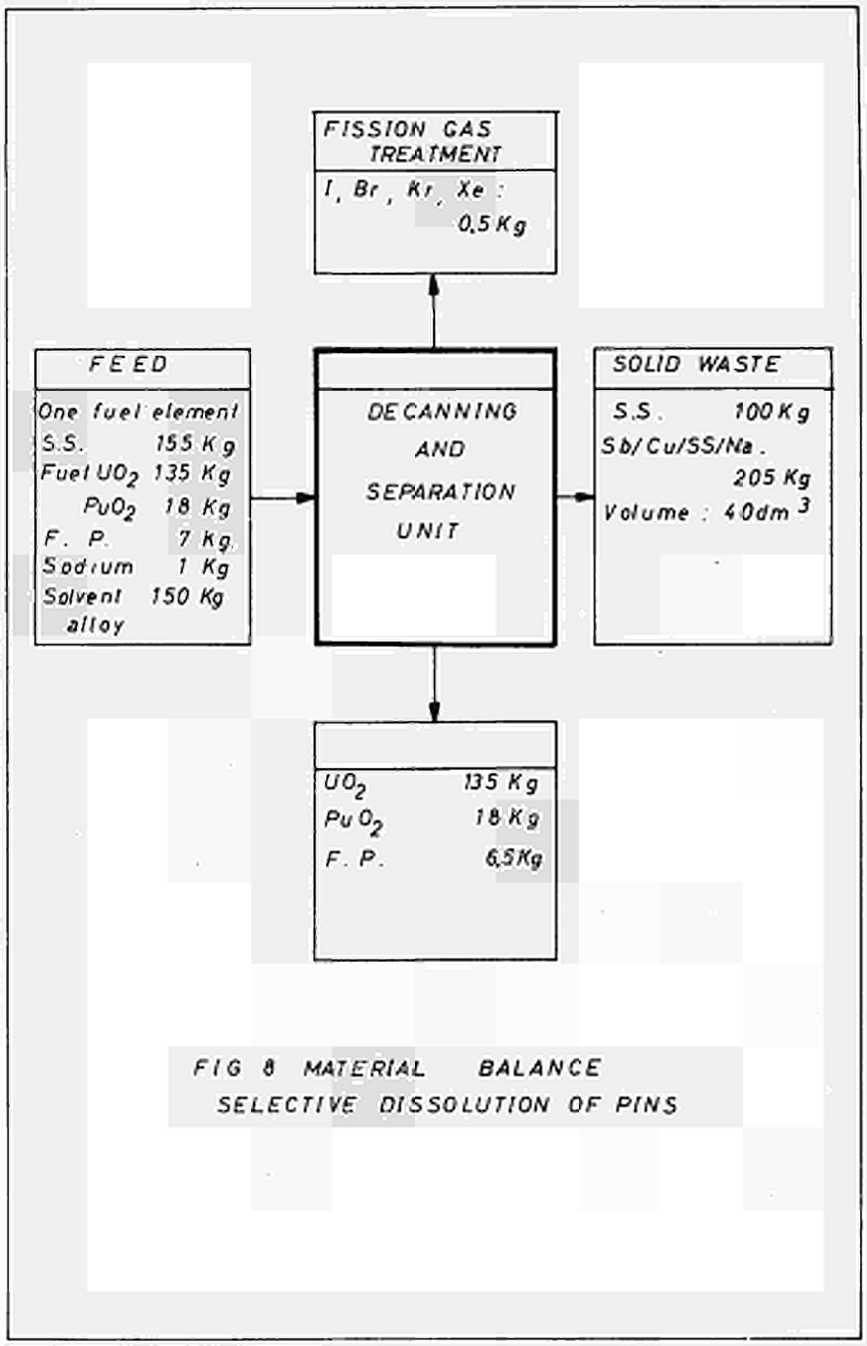


FIG 8 MATERIAL BALANCE
SELECTIVE DISSOLUTION OF PINS

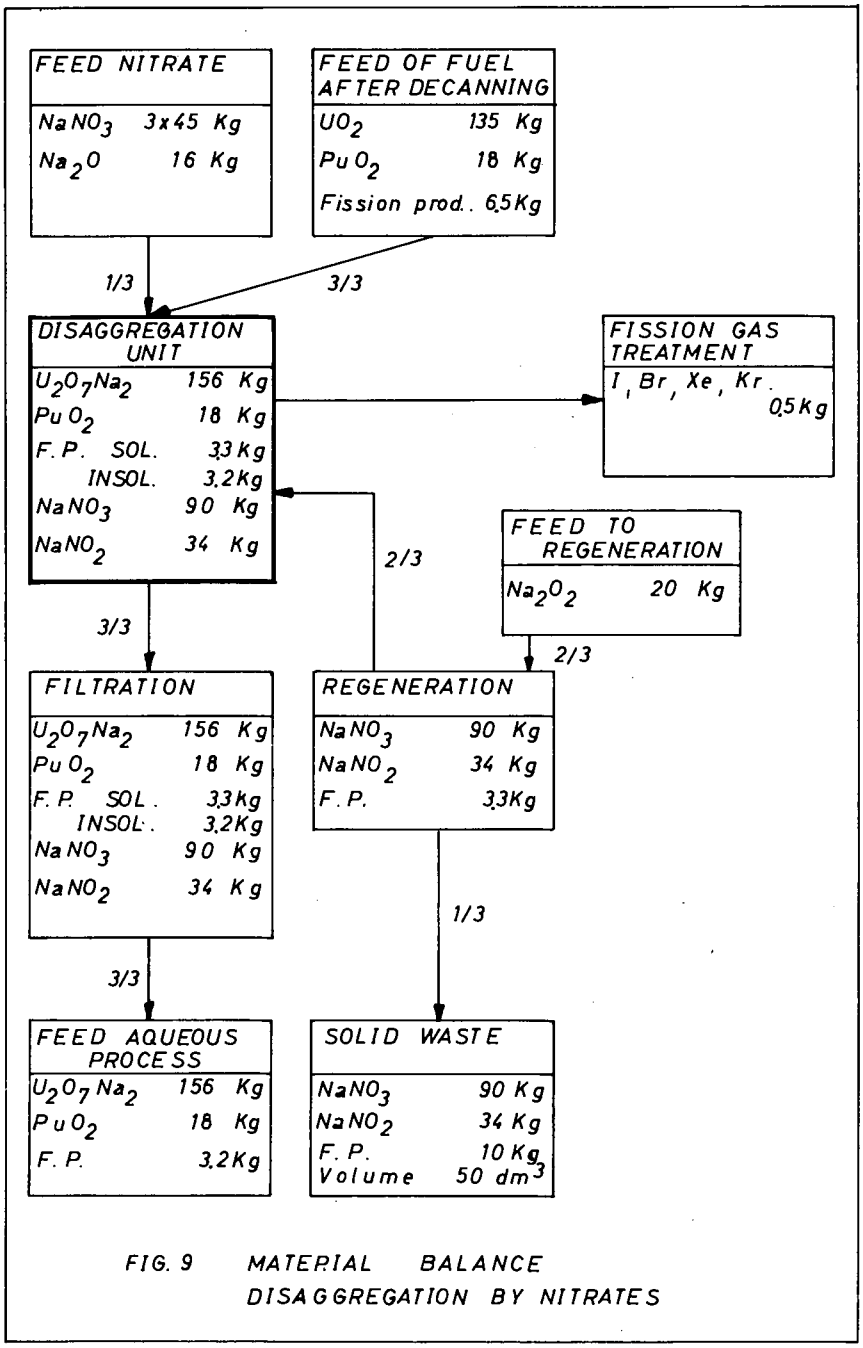
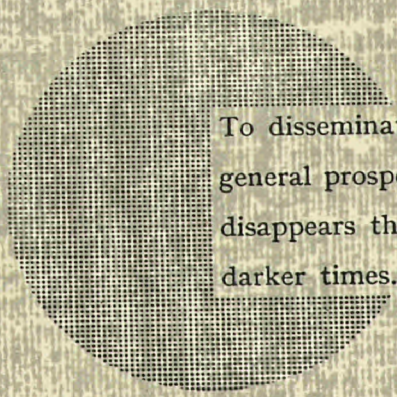


FIG. 9 MATERIAL BALANCE
DISAGGREGATION BY NITRATES



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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