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Chemical aspects in the design of a flowsheet for a large-scale LWR reprocessing plant*

Chemische Aspekte beim Entwurf eines Fließschemas einer großen Wiederaufarbeitungsanlage für Brennstoffe aus Leichtwasserreaktoren

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Abstract

A reference flowsheet for a 1500 tons per year LWR-fuel reprocessing plant was prepared in 1974. The present paper discusses several process alternatives for the chemical main process, and the criteria used in the selection of specific procedures for fuel dissolution, dissolver off-gas treatment, separation of uranium and plutonium from fission products, uranium-plutonium partitioning, and purification of products.

1. Introduction

In the frame of the Projekt Wiederaufarbeitung und Abfallbehandlung (PWA) of the Gesellschaft für Kernforschung a reference flowsheet for a 1500 tons per year LWR reprocessing plant was designed in 1974, in a cooperation with the companies KEWA, GWK, and Uhde-Lurgi-St. Gobain. In the meantime several improvements and additions to this so-called Mark I flowsheet have been made. Major consideration during the development of the flowsheet has been directed towards

– high safety and reliability of operation,
– high plant availability,
– minimization of waste volumes to be handled,
– minimization of environmental burdens caused by releases of radioactive effluents.

The measures taken to accomplish these conditions can very broadly be described as

– use of proved techniques, as far as available, eventually after adequate adaptation to the special requirements of LWR fuel reprocessing,
– introduction of new techniques where the present technology has not or not completely been satisfactory.

The present paper discusses, from a chemical point of view, the selection of several steps in the chemical main process, which comprises the so-called *chemical head-end* (fuel dissolution and off-gas treatment) and the *plutonium-uranium raffination by extraction* (PUREX process). General reviews of nuclear fuel reprocessing [1–3] and discussions of the present state of knowledge in LWR fuel reprocessing [4, 5], of extraction equipment [6], and of several chemical engineering aspects [4, 7] have appeared elsewhere.

The basic fuel data used in the reference flowsheet have been: an initial enrichment of 3,6 % ^{235}U for "normal" fuel, or of 3 % Pu_{fiss} in natural U for plutonium recycle fuel; a maximum burn-up of 40 000 MWd/t; and a minimum cooling time of 200 d. The plant throughput has been assumed as 5 t uranium per day, with a load factor of 0,83.

2. Head-end treatment

2.1. General requirements

In the design of a flowsheet for fuel dissolution and head-end off-gas treatment three requirements should be observed:

– Iodine should be removed – if possible completely – from the dissolver product solution in order to prevent its spreading over other parts of the plant and, hence, to avoid the necessity of iodine retention in the off-gas systems of those parts of the plant.

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– Tritium should be limited to the head-end and to the high-activity part of the extraction system in order to minimize the amount of water contaminated by tritium.
– The amount and composition of the head-end off-gas must be carefully controlled in order to obtain optimum conditions for the removal of ^{129}I, ^3H, and ^{85}Kr.

Based on the initial Mark I head-end flowsheet [8], an improved off-gas treatment scheme has meanwhile been worked out, partly in cooperation with the French C.E.A.

2.2. Fuel dissolution

The chop-and-leach process which consists of chopping the fuel element rods mechanically into short pieces and then leaching the fuel with nitric acid from those pieces has been chosen for breakdown of the spent fuel elements. Chemical decladding procedures as used by the Eurochemic plant [9] have turned out to suffer from excessive waste production and from product losses.

The dissolution of UO_2 fuels with nitric acid does not offer major problems. Even with LWR fuels of very high burn-up (36 000 MWd/t fuel from the Obrigheim PWR), dissolution was essentially complete after 4 h leaching with boiling 6 M HNO_3 [10]. In contrast, the dissolution behaviour of plutonium recycle fuels fabricated by *mechanical blending* of PuO_2 and UO_2 is not at present sufficiently known. There is a danger that during reactor operation this fuel may not be completely transformed into $(U,Pu)O_2$ solid solution and, hence, that complete dissolution of the plutonium may not be accomplished with semi-concentrated nitrite acid. A systematic study of the behaviour of this type of fuel will therefore be made in the near future. With regard to PuO_2-UO_2 fuels fabricated by *coprecipitation* of the components, preliminary results with FBR fuel (Dounreay, 61 000 MWd/t, ca. 15 % PuO_2) indicate a satisfactory dissolution behaviour with nitric acid [10], but a more systematic study also here is important.

The insoluble residues remaining after fuel dissolution have been measured during several experiments in the MILLI experimental facility of the Institut für Heiße Chemie, and have amounted to about 0,5 weight-% both with LWR and with coprecipitated FRB fuels [10]. The residues consisted mainly of oxidic and metallic fission product particles and of fines from the cladding material; the fissile materials content was very low, about 0,04 % each of the total amount of U and Pu. The loss of plutonium remaining with the cladding hulls was of the same order of magnitude.

It should be pointed out that effective removal of the highly radioactive fine particles from the dissolver solution by filtration or centrifugation is of great importance for a smooth

operation of the first extraction cycle, in order to suppress the "crud" formation (see below for a discussion of this effect).

2.3. Iodine removal

During the dissolution of the fuel by nitric acid the gaseous and a part of the volatile fission products are released to the off-gas. Moreover nitrous oxides are produced by reaction of UO_2 with HNO_3 according to the simplified equation,

$$2UO_2 + 6HNO_3 \rightarrow 2UO_2(NO_3)_2 + NO_2 + NO + 3H_2O,$$
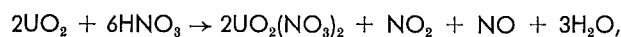
and are released to the off-gas.

Removal of iodine from the dissolver solution can be attained by "stripping" this element, in the form of I_2, by vapour or air. In both cases the total amount and the flow rate of the stripping gas must be sufficiently high in order that the desired decontamination factor (DF) is obtained. Because of the temperature dependence of the distribution coefficient of iodine, and in order to keep the amount of off-gas to a minimum, iodine is best removed during the dissolution process itself, using the vapour of the boiling solution as the stripping gas. This means that the dissolution is not carried out under reflux in order that a reflux of the iodine with the condensate is prevented.

The efficiency of the iodine removal may be limited by two reactions:

- oxidation of iodine to non-volatile iodic acid by boiling nitric acid,
- reaction of iodine with organic materials (such as degradation products from the organic solvent used in the solvent extraction part which can be introduced with recycled acid, or lubricating greases from the shear machine).

The first reaction becomes important towards the end of the dissolution when the concentration of nitrous oxides (which are reductants for iodic acid and hence prevent its formation) is decreased. This can be counteracted by the addition of sodium nitrite or, preferably, gaseous NO_2 at the end of the dissolution, as has successfully been demonstrated in preliminary experiments at Marcoule [11]. The second reaction can lead to a lower iodine removal from the dissolver or may produce organic iodine compounds which are more difficult to retain from the off-gas. This calls for an improved treatment of the recycle acid, and may require constructive modifications of the shear machine.

2.4. Confinement of tritium

During the chop-and-leach procedure tritium is essentially released as tritium-water, HTO, to the dissolver solution. Only less than 1 % of the total tritium are released as hydrogen gas (HT or T_2) [12] while a larger amount of tritium which is not exactly known at present remains in the zircaloy cladding of the LWR fuel pins. Consequently the tritium which is released follows the aqueous phase, and can be removed from gas streams simply by condensation.

In order to prevent its spreading over the lower-activity parts of the plant, a special "tritium scrub" with freshwater is applied in the first extraction cycle, see Section 3.2. In order to minimize the volume of tritiated water, water and acid from the head-end and from the high-activity extraction cycle must be recycled, while the feed of freshwater to this part of the plant must be kept to a minimum. This can for instance be attained by introducing the acid needed for dissolution in the form of fuming nitric acid (23 M HNO_3) or of N_2O_4 [30].

2.5. Head-end off-gas treatment

The off-gas coming from the shear machine is preferably drawn through the dissolver in order to dissolve radioactive dust particles carried by the gas. The off-gas from the dissolver is composed of air or nitrogen used as purging gas for the shear, nitrous oxides from the dissolution process, and gaseous fission products which may amount up to a few volume-%. In addition radioactive aerosols mainly from the dissolver are carried by the off-gas stream. For the removal of the radiotoxic components, and of components interfering with the removal procedures (i.e., the nitrous oxides), the following sequence of gas cleaning steps has been selected:

- Removal of nitrous oxides by washing with water or dilute nitric acid in the presence of sufficient oxygene (recombination to nitric acid).
- Filtering of aerosols by a sequence of filters of increasing filtering power [13].
- Removal of iodine by sorption on AC-6120, a silver-impregnated catalyst carrier material [13].
- Removal of krypton by low-temperature distillation [14].

For an undisturbed operation of this system, several additional procedures are included into the flowsheet. In the recombination step, between about 20 and 50 % of the iodine remain in the recombined nitric acid [11]; depending on the mode of acid recycle, this amount must be lowered or even totally removed by an additional iodine stripping step before the acid is recycled. In the low-temperature distillation process, any components which would freeze out of the gas stream in the distillation columns must before be removed. Moreover due to the radiolytic formation of ozone from oxygen by the ^{85}Kr β radiation, it is necessary to remove the oxygen in order to prevent an accumulation of ozone. This is attained by a catalytic "burning" of oxygen and nitrous oxides with added hydrogen gas. The water thus produced is condensed from the gas stream which is further purified from interfering components (CO_2, residual H_2O and NO_x) by a molecular-sieve bed.

3. First extraction cycle

3.1. Impact of the criticality safety concept

Criticality control is an extremely important point to be observed in a reprocessing plant. Particular problems arise in those parts of the facility where plutonium and uranium are not yet separated from one another, i. e., in the head-end part and in the co-extraction cycles; the reason is that, at least hypothetically, there is a possibility that a (unintentional) separation of plutonium from uranium and, hence, an accumulation of plutonium in critical concentrations might occur in certain equipment of those parts of the plant. (For a basic discussion of criticality see [15].) The criticality safety concept applied must guarantee that a criticality accident can by no means occur.

In the original Mark I flowsheet, addition of gadolinium nitrate as a »soluble neutron poison« to the dissolver acid was proposed for criticality control of the dissolver. This has immediate implications to the solvent extraction parts because

- the soluble poison is introduced with the dissolver product solution into the first extraction contactor,
- consequently, it is reasonable to use homogeneous poisoning for criticality control of all extraction equipment where plutonium and uranium have not yet been separated from one another,

- the product elements, uranium and plutonium, must effectively be decontaminated from the soluble poison in the course of the extraction process in order to meet the product specifications.

Calculations have shown that a decontamination factor (DF) of plutonium for gadolinium between 10^4 and 10^5 is needed to meet product specifications, a value which conceivably cannot be guaranteed routinely with one purification cycle. This means that two purification cycles are needed to clean the products from gadolinium. Since, on the other hand, three extraction cycles in total are needed to meet the product specifications with regard to fission products (DF ca. 10^7), it follows that only the first of these cycles can be allowed to be homogeneously poisoned, and this in turn means that the plutonium-uranium separation must be performed in the first cycle.

Very recently, a cooperation between Gesellschaft für Kernforschung and Metallgesellschaft has led to the proposal to use hafnium metal as a neutron-absorbing construction material for certain equipment in reprocessing [16]. Although this material is not at present licensed by the public authorities as a construction material in apparatus design, there is good reason to believe that licensing conditions can be met. With sieve-plate columns fabricated from hafnium additional homogeneous poisoning of the extraction columns by gadolinium nitrate or other soluble poisons would not be necessary. Consequently other considerations would then become dominant for the arrangement of the plutonium-uranium separation (first or second cycle). A »late« separation would save one of the plutonium purification cycles, and would perhaps be favourable with regard to operational reliability since the influence of radiolysis products (nitrous acid, dibutyl phosphoric acid) on this step would be much lower in the second cycle; on the other hand, an "early" separation would be favourable with regard to an optimum layout of the flowsheet for product purity (in particular uranium purification from neptunium and plutonium). A thorough reconsideration of this question under the "hafnium aspect" has not up to now been made.

3.2. Extraction and scrub

The particular problems with fuels of high burn-up origin from the very intense radiation of the fission products. Consequences are

- a relatively high production rate of radiolysis products from the organic solvent, in particular of di- and monobutyl phosphoric acids (HDBP and H_2MBP), which in combination with certain fission products (in particular zirconium) lead to the formation of insoluble, slimy interphase precipitates ("crud"),
- losses of plutonium with the spent organic solvent caused by complexation with HDBP and with certain solvent radiolysis products which are not removed by the usual solvent wash procedures [17],
- losses of plutonium with the high-activity waste (HAW) caused by radiolytic formation of "inextractable" plutonium species, and by a loss of efficiency of the extraction equipment due to crud formation.

As an example for these effects, experience in the WAK pilot reprocessing plant at Karlsruhe may be cited where, with fuel of 15 000 to 20 000 MWd/t burn-up, severe hydraulic failures and finally blocking of the first mixer-settler battery by interfacial cruds, combined with increased product losses, occured which eventually forced to shut-down operation [18].

Although these difficulties in the WAK have been overcome by the installation of an improved HA mixer-settler battery [19], this experience, in combination with experience gained at the Eurochemic plant at Mol, Belgium, [20], has led to the conclusion that pulsed columns are superior to mixer-settlers in a high-activity extraction cycle. An additional, chemical, means of improvement has been demonstrated very successfully with fuels up to 61 000 MWd/t burn-up in the MILLI facility; it consists of increasing the metal loading of the organic phase (i. e., the solvent saturation with uranium and plutonium) from the usual ca. 60 % to a value of 75 to 80 %, which is performed by proper adjustment of the feed-to-solvent flow ratio and by an increase of the aqueous acidity to about 3 M HNO_3 [10]. With these modifications, only very slight formation of cruds without any operational perturbations were observed although the mixer-settlers of the MILLI, due to their small size and special design (critically ever-safe "slab" geometry), are hydraulically unfavourable. An unequivocal explanation of the chemical reasons for this effect has not up to now been offered but we believe that it can be found by the following – simplified – considerations:

- the increased uranium concentration in the organic phase leads to a higher consumption of both TBP and HDBP for uranium complexation and, hence, to a lower availability of these complexants for fission product Zr, i. e., the distribution coefficient of Zr is strongly decreased;
- the increased acidity of the aqueous phase decreases both the amount and the rate of formation of solid "zirconium dibutyl phosphate", a material which contains zirconium and dibutyl phosphate in the ratio 1:2 and in addition an unknown amount of nitrate anions [21].

In the Mark I flowsheet, the uranium concentration in the organic phase at the organic outlet of the first (HA) extraction column has accordingly been set to 95 g U/l which corresponds to ca. 75 % solvent saturation, and the HNO_3 concentration in the aqueous feed solution has been set to ca. 3 mol/l. Other specific features of this flowsheet are:
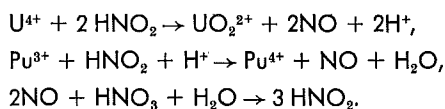
- A "double scrub" is used for optimum removal of fission products. The first scrub, performed in the upper part of the HA column, is done with ca. 4 M HNO_3 in order to remove preferentially ruthenium while the second, with 1,5 M HNO_3, is performed in an additional HS column for preferential removal of zirconium.

- A "freshwater" scrub with fresh (non-recycled) nitric acid is additionally included to remove tritiated water and acid from the organic solvent, with the aim to confine the tritium in the high-activity parts of the plant [30], see Section 2.4. This tritium scrub must be performed at a very high organic-to-aqueous flow-ratio which poses difficulties with regard to the extractor to be used.

The flowsheet – except the extra tritium scrub which is not foreseen in the MILLI – has successfully been tested with 36 000 MWd/t fuel from the Obrigheim KWO reactor in the MILLI [10], with the following essential results: DF (gross γ) = 10^4; DF (Ru) = 500 to 1000; Pu losses to HAW 0,1 %; unexpectedly low HDBP formation of ca. 30 mg HDBP per liter of solvent; smooth performance of the extractors during the entire 100 h campaign.

3.3. Uranium-plutonium partitioning

The procedures presently in use are reduction of the plutonium to the +3 state with ferrous sulfamate or with uranium (IV) nitrate/hydrazine. Both techniques cannot be considered

to be completely satisfactory. With ferrous sulfamate, chemical and radiative decomposition of the sulfamate anion leads to the formation of sulfuric acid in the medium-active waste (MAW) from the second plutonium cycle which poses severe corrosion problems in the concentration and solidification of this MAW; moreover the iron burden to this MAW is another disadvantage. Ferrous sulfamate is therefore not any longer considered as a choice for LWR reprocessing plants. With uranium(IV) nitrate/hydrazine, the large excess of reductant necessary (at least 10-fold of the stoichiometric amount of U^{IV}) is a major drawback in particular with fuels of high plutonium content, resulting in the need to increase the throughput of the uranium line of the plant substantially, and in a change of the residual enrichment of the fuel uranium if uranium is used as the reductant which does not originate from the same fuel charge. The particular problem is, however, that with high-burn-up fuels occasionally a tendency to failure of the process has been observed. The reason for this failure is not completely known but is presumably due to excessive formation of nitrous acid in the HA contactor; the HNO_2 is extracted by TBP and introduced into the partitioning contactor, where the U^{IV} and Pu^{III} are reoxidized by an autocatalytic reaction, according to the following (simplified) equations:

$$U^{4+} + 2\,HNO_2 \rightarrow UO_2{}^{2+} + 2NO + 2H^+,$$

$$Pu^{3+} + HNO_2 + H^+ \rightarrow Pu^{4+} + NO + H_2O,$$

$$2NO + HNO_3 + H_2O \rightarrow 3\,HNO_2.$$

Excessive consumption of U^{IV} or re-oxidation of Pu^{3+} has for instance been observed during test operations in the Hanford Purex Plant [22] and during normal operations in the WAK [23]. In the MILLI, up to the 25-fold stoichiometric excess of U^{IV} has occasionally been necessary to keep the process running [10].

For the Mark I flowsheet we consequently have proposed to use the electrolytic in-line reduction process which was first developed at Karlsruhe [24]. For the application of this procedure in a pulsed column, a special construction ELKE (electrolytic column for extraction) which does not make use of a diaphragm has been developed [25]. The advantages of the electrolytic process lie in the fact that no additional chemical reagents are used (except hydrazine which acts as a "nitrous acid destroyer" but which is easily decomposed into gaseous products during re-oxidation of the plutonium product, see below), and that a very fast and direct control of the process – by control of the electric current supplied – is possible. The diaphragm-free version of the process has the additional advantage that plugging of the pores of a diaphragm, which may be possible by the action of crud-type materials, cannot occur. The electrolytic process has been intensely tested in an electrolytic mixer-settler in the MILLI [25, 26], even with FBR fuel of 61 000 MWd/t burn-up and 15 % PuO_2 content [10]; the results with regard to product recoveries, product purities, and smoothness of operation have been very good in all cases. It is interesting to note that a similar electrolytic U/Pu separation, however using a diaphragm [27], will be applied in the Allied-Gulf 1500 tons-per-year plant presently under construction near Barnwell, South Carolina, USA.

3.4. Re-extraction and solvent clean-up

No major problems are inherent to the uranium re-extraction; a temperature of ca. 60 °C is foreseen for the strip solution in order to obtain a high uranium concentration in the product solution.

The spent organic solvent is washed in order to remove decomposition products, in particular HDBP and H_2MBP. The present procedure which uses Na_2CO_3 or $Na_2CO_3/NaOH$ solutions is by no means satisfactory since due to the high salt content (mainly $NaNO_3$, produced from reaction of Na_2CO_3 or NaOH with the residual HNO_3 of the spent solvent), the spent wash solutions form an important part of the non-concentratable medium-active waste. A "salt-free" process has been developed at Karlsruhe [28] which uses hydrazine hydrate as the alkaline washing agent, and electrolysis to decompose the hydrazine nitrate of the spent wash solution into gaseous products. In addition, a fixed-bed PbO_2/SiO_2 column is included for oxidative break-down of those radiolysis products which are not removed by alkaline washing. The process will be described in more detail in a later issue of "Kerntechnik" [28].

4. Uranium purification cycles

Most of the existing reprocessing plants use intercycle evaporation of the first-cycle uranium product solution to prepare a concentrated feed solution for the second extraction cycle. However with an adequate adaptation of the flowsheet it is possible to start directly with the "dilute" uranium product solution (ca. 80 g/l U) and to avoid intercycle evaporation. After a thorough consideration of the advantages and disadvantages of the "dilute" and "concentrated" modes of extraction (Table) we concluded that the advantages were more in favour of the "dilute" flowsheet which consequently has been incorporated for the second and third uranium cycle of the Mark I flowsheet.

Table: "Concentrated" vs. "dilute" flowsheet for uranium purification

Advantages of concentrated flowsheet
1. Lower feed throughput (reduction of total liquid throughput in the A column by about 30 %)
2. Slightly higher uranium loading of solvent attainable (ca. 95 g/l vs. ca. 80 g/l)
3. Ruthenium decontamination is said to be improved after evaporation[1] (?)

Advantages of dilute flowsheet
1. Saving of uranium intercycle evaporator.
2. Saving of kerosene wash of the first-cycle uranium product.
3. No formation of Np (VI) during evaporation (improvement of Np decontamination expected).
4. Improvement of fission product decontamination expected due to lower (more favourable) organic-to-aqueous flow-ratio.

[1] Ruthenium decontamination factors necessary to meet specifications are routinely obtained without intercycle evaporation in the MILLI.

The second uranium cycle, besides purification from residual fission products, is specifically designed for purification from plutonium; for this reason some U^{IV} nitrate + hydrazine is added to the 2A column to reduce the plutonium to the inextractable +3 state. The third uranium cycle is specifically designed for purification from neptunium. A total DF of uranium for neptunium greater than about 500 is necessary in order to meet specifications (1500 desintegrations of ^{237}Np per minute per gram of U). Since the first cycle only yields a very moderate DF for neptunium (MILLI: DF (Np/U) = 1,3 to 2; DF (Np/Pu) = 2,6 to 5), decontamination from this element must be performed in the purification cycles. Removal of Np can be improved by addition of sufficient nitrous acid (preferably as NO_2 gas) but the absolute necessity of this (inconvenient) measure is not at present assured. In the MILLI, tests of the second U cycle flowsheet (with addition of U^{IV}) yielded DF (gross γ) = 25 to 90, DF (Pu) = 3×10^2 to 1×10^3, DF (Np) = 10 to 125; for the third cycle, with addition of NO_2^-, a DF (Np) of 70 to 250 was obtained [10].

5. Plutonium purification cycles

Plutonium is obtained in the +3 state in the first-cycle product solution, and must be re-oxidized to Pu^{4+} for second-cycle extraction. The procedures presently in use — oxidation with sodium nitrite or with NO_2 gas — are not satisfactory since with the $NaNO_2$ process a salt-containing MAW is produced in the second Pu cycle while with the NO_2 process extensive off-gas cleaning is needed. These disadvantages are not inherent to the continuous electrolytic re-oxidation process (»ROXI«) developed at Karlsruhe [25] which has been proposed for the Mark I flowsheet.

In view of the problems connected with plutonium evaporation (irreversible formation of plutonium polymer and of solid plutonium deposits, criticality problems), the second and third plutonium cycles are designed to avoid plutonium intercycle or final product evaporation. A plutonium final product solution with a Pu concentration sufficient for direct oxalate precipitation, i. e., with $\geq$ 60 g Pu/l, can be obtained by use of a reductive re-extraction of the plutonium from the organic solvent. Since the Pu^{3+} distribution coefficients are much lower than those for Pu^{4+}, a much lower aqueous-to-organic flow ratio can in this case be applied, leading to a corresponding concentration factor in the re-extraction contactor. This is of particular importance since in the extraction contactor the concentration factor attainable is limited by the fact that the plutonium loading of the organic solvent must be limited to < 40 g Pu/l, because of the danger of third-phase formation at higher loadings in the system $Pu(NO_3)_4$-HNO_3-H_2O-TBP-n-alcane [29]. With the electrolytic plutonium re-extraction process developed at Karlsruhe [25], third-cycle plutonium product concentrations of $\geq$ 60 g Pu/l are obtained (as compared against the $\leq$ 15 g Pu/l attainable by non-reductive flowsheets) with very low losses of plutonium to the spent organic solvent.

Due to the lower loading of the organic solvent (see above), the decontamination factors attainable in the plutonium purification cycles are lower than those for the uranium cycles, but are sufficient to meet specifications. Similar to the uranium case, Np decontamination can be improved by addition of nitrous acid (preferably as NO_2). Tests in the MILLI gave for one purification cycle (with $NaNO_2$ addition) DF (gross γ) = 25, DF (Np) = 330. (Received on 15. 3. 1976)

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