RADWASTE SOLIDIFICATION MODIFICATIONS BY MEANS OF

NITROGEN OXIDES CATALYTIC ABATEMENT

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ABSTRACT

In the treatment and solidification of medium and high level radioactive wastes, large amounts of NO_x are produced, which are normally scrubbed with nitric acid or alkaline solutions. In this way big volumes of secondary wastes containing high nitrate concentrations which cannot be easily discharged are produced. The application of the NO_x catalytic abatement with selective ammonia reduction would permit to avoid this problem, with large cost savings. Two practical examples have been examined: a bituminization plant and a pot vitrification plant referred to the Italian EUREX Reprocessing Pilot Plant. 416,000 and 362,000 $/y respectively would be saved by replacing scrubbing towers with a catalytic reactor.

INTRODUCTION

In the treatment and solidification of medium and high level radioactive wastes, large amounts of nitrogen oxides are produced. These gaseous oxides, generally named NO_x, are normally composed of NO and NO_2, with sometimes small amounts of N_2O.

The NO_x are generated in the radwaste treatment during the wastes concentration step, before their solidification, when organic reductants such as formaldehyde or formic acid are added in order to lower the nitric acid concentration. Moreover, during the calcination or the vitrification of the concentrated high level wastes all the nitrates are also decomposed to NO_x. In such a manner the gas leaving the treatment and the solidification steps contains up to several percent of NO_x, and requires an additional treatment in order to recover the nitric acid and to lower the NO_x concentration below the limits established for the discharge to the atmosphere.

The method most used for this treatment consists of gas scrubbing by means of cooled water and/or diluted nitric acid, if the recovery of nitric acid is needed, or by means of alkaline solutions. The efficiency of the NO_x removal using these methods is, in the best operational conditions and with well designed apparatus, of the order of 90%, being much lower, that is 60 ÷ 70%, in several cases (1) (2) (3). Moreover, the use of the absorption technique gives rise to considerable amounts of secondary radioactive wastes, containing relatively high concentrations of nitrates, which in turn are to be treated and conditioned if they cannot be discharged as is the case when they do not fulfil the requirements of the environment protection laws against the chemical pollution.

In order to overcome these problems the use of the catalytic selective abatement of the NO_x with ammonia is under consideration at ENEA in Italy. The chemical reduction of the NO_x to Nitrogen and water, which can be performed at efficiencies higher than 99%, can strongly reduce both the amounts of the chemical salts to be discharged in the water bodies, and the amounts of NO_x in the atmosphere.

THE CATALYTIC REDUCTION OF NO_x WITH AMMONIA

The catalytic reduction of NO_x with ammonia is a process under development at a pre-industrial stage in several laboratories and industries (4) (5) (6). The NO_x abatement is accomplished according to the following main chemical reactions:

$$6\,NO_2 + 8\,NH_3 \longrightarrow 7\,N_2 + 12\,H_2O$$
$$6\,NO + 4\,NH_3 \longrightarrow 5\,N_2 + 6\,H_2O$$

over Hydrogen Mordenite extrudates (Zeolon 900 H, a product of Norton Chemical Co).

According to our laboratory studies, in order to obtain high NO_x removal efficiencies, the operational conditions must be well controlled. The catalytic reactor must be maintained at 450°C, the residence time of the gases in the reactor must be at least 0.2 sec., the gas velocity through the reactor must be of the order of 1.5 ÷ 2.0 m/sec. Moreover, the vapour concentration in the gas feed to the reactor is very important also. To obtain efficiencies higher than 99% it must be maintained below 60% v/v.

Another aspect to be considered is the possible presence of unreacted ammonia in the off gas. It must be reduced as much as possible for two main reasons: first, because of the low ammonium salts concentrations established by the Italian law for the discharge of chemical wastes; second, to avoid the formation, deposition and possible detonation of ammonium nitrate. In order to fulfil these requirements, the ratio NH_3/NO_x must be 1.0 ± 0.1, and the ammonia gas addition must be interlocked to the bed temperature and controlled by the NO_x concentration.

DISCHARGE LIMITS OF NITRATES AND AMMONIUM SALTS IN ITALY

The discharge of the liquid wastes into rivers is permitted in Italy only if the concentrations of the chemical pollutants are below the limits established by law [7]. In the case of the Nitrogen compounds these limits are the following:

NO_3^-	: 20 mg/l as Nitrogen 121 mg/l as $NaNO_3$
NO_2^-	: 0.6 mg/l as Nitrogen 3.0 mg/l as $NaNO_2$
NH_4^+	: 15.0 mg/l

It must be observed that it is not permitted to dilute the wastes with fresh water in order to comply with these limits.

APPLICATION OF THE NO_x CATALYTIC ABATEMENT TO THE RADWASTE SOLIDIFICATION PLANTS

In order to evaluate the advantages which can be obtained using the NO_x catalytic abatement, we refer to the Italian Reprocessing Pilot Plant EUREX and to the radwaste solidification plants whose construction is being considered at the same site: a solidification plant for the medium-low level wastes, and a vitrification plant for the high level wastes.

The EUREX plant, which is located in Northern Italy, discharges the liquid low level radwastes to the Dora River, in compliance with the radioactivity discharge limits established by the Authorities. The wastes, before discharge, are collected in two ponds each of 1000 m^3, where they are diluted and controlled. These ponds collect all active low-level or non active wastes, and each of them is drained off about 25 times per year at the most. Therefore a maximum of about 50,000 m^3 of diluted wastes is discharged to the river each year.

Application to the medium and low level waste solidification

For the solidification of low and medium level wastes the bituminization process has been taken into consideration since 1975. In order to be solidified, in this case the wastes must be treated to reduce their volume before feeding then to the extruder machine. The flow sheet designed for this pretreatment is shown in Fig.1. According to it, the waste called (A+B) is concentrated and denitrified by means of formaldehyde, then the concentrate goes to the extruder, while the NO_x containing gas is scrubbed with an alkaline solution. Assuming that the scrubbing efficiency is about 94%, 590 m^3/y of liquid secondary wastes will be produced, containing 112 g/l of $NaNO_3$.

Although the low specific activity would permit their direct discharge to the river, in order to comply with the pollution control law these secondary wastes will have to be diluted 926 times (dilution factor = 926). For this operation 7280 m^3/d of dilution water would be needed on the average, for a total of about 0.5 x 10^6 m^3/y while, as said before, the EUREX Plant discharges at present a maximum of 140 m^3/d and a total of 50,000 m^3/y.

In conclusion, according to the flow-sheet, only a maximum of 2.3% of secondary wastes could be discharged to the river while the 97.7%, that is 576 m^3/y, would have to be conditioned in some way. A theoretical possibility to avoid the conditioning of the secondary liquid wastes could be to transport and to discharge them to the sea, but many practical, economical and political problems would arise in this case. So this hypotesis at present cannot be taken into consideration.

Taking into account the radioactive contamination, the best method for the conditioning would still be the bituminization, increasing the production capacity of the extruder, and producing in this way about 576 drums (d = 1.4 g/cm^3, 40% w/w of waste salts) in addition to the about 600 primary drums per year.

The need to solidify the secondary wastes would be eliminated if the alkaline scrubbing is replaced by the NO_x catalytic abatement, according to the flow sheet shown in Fig. 2. In this scheme the catalytic reactor is placed between the evaporator-denitrator and the condenser, and the NO and all the vapour pass through it. In order to lower the vapour concentration, some dilution air is necessary, while the ammonia feed respects the NH_3/NO ratio = 1.0.

In these conditions, in laboratory scale experiments we obtained abatement efficiencies of the order of 99.5-99.8%. Assuming that the efficiency, in the real plant conditions is only 99%, the 420 m^3/y of secondary wastes, that is the condensate, could be now discharged to the river after a 73 times dilution without problems, as the maximum dilution factor which could be obtained at the EUREX Plant for these wastes is about 120.

Application to the Vitrification Plant

The IVET Process [9], based on the pot vitrification concept, has been developed by ENEA as a possible way to vitrify the high level wastes produced and stored at the EUREX Plant. The flow sheet of the IVET Process, referred to the vitrification of HLW from PWR fuel is shown in Fig. 3. There are two **evaporator-denitrators** where NO_x gases are produced: the first used for the HLW coming from the tanks, the second for the concentration and denitration of the distillates and of the scrubbing towers water.

The other source of NO_x is the vitrification pot, where all nitrates are decomposed. Four scrubbing towers are foreseen to scrub the gas, the last one acting to lower the NO_x concentration to negligible values. The acid produced in the third scrubbing tower is neutralized and, taking into account its low specific radioactivity, could be considered low level waste to be discharged.

In this case also, just as in the case of the bituminization process, the discharge of this LLW to the river cannot be performed because of the high nitrate concentration. It would be necessary in fact to dilute it 641 times before the discharge, when the maximum dilution factor could be 62. Only the 9.8% of this waste therefore could be diluted and discharged while the 90.2%, that is 720 m^3/y, needs to be conditioned. Its bituminization would produce about 500 additional drums requiring of course storage, transport and disposal.

The situation is completely different when the selective NO_x abatement replaces the last two scrubbing towers, as shown in Fig. 4. The condensate from the catalytic reactor, that is 584 m^3/y, can be discharged at a dilution factor of 53, being possible to dilute it with the existing ponds up to 86 times.

OPERATIONAL COST SAVINGS WITH THE NO_x CATALYTIC REDUCTION

In order to evaluate the savings in dollars due to the NO_x catalytic abatement, we will not take into account, as a first approach, the NO_x reactor installation cost compared to the scrubbing towers installation cost, assuming that the two systems cost about the same. Moreover, we will not consider other possibilities for the secondary waste solidification besides their bituminization with the same plant.

The additional costs of this option can be calculated taking into account the cost of:
- the bituminization
- the transportation of the solidification wastes
- the burial

As at present there do not exist yet in Italy either industrial bituminization plants, or national disposal sites, therefore for the cost evaluation we have to refer to data available in literature.

The bituminization cost was evaluated in Belgium in 1976 (10) of the order of 2500 $\$/m^3$ of treated waste, excluding investments, while it was about 3200 $\$/m^3$ of treated waste in USA with reference to 1980 (11) (12) that is 640 $/drum.

The shipping charges in USA in 1980 were evaluated as high as 1500 $ each 60 drums having an external dose from 0 to 0.2 R/h, that is 1500 $/Trip and 25 $/drum (11).

The burial charges, for the same conditioned waste category from 0 to 0.2 R/h, were in USA, always in 1980 (11):

Burial : 6 $\$/ft^3$ that is 42.4 $/drum
Perpetuity : 0.75 $\$/ft^3$ that is 5.3 $/drum
Decommissioning : 0.78 $\$/ft^3$ that is 5.5 $/drum
Cask handling : 210 $/Cask minimum
Business License Tax : 2.4% to total of all disposal fees.

The total cost was about 58 $/drum.

In Europe the cost of the disposal charged to the French ANDRA's customers was in 1981 of 300 $\$/m^3$ of conditioned LLW disposed in tumuli (13), that is 60 $/drum.

In conclusion, referring to the year 1980 prices, each additional drum of bituminized waste will cost:

- production	: 640 $
- transportation	: 25 $
- burial	: 58 $
Total	: 723 $

The application of the NO_x catalytic abatement to a bituminization plant of the type to be built, if that will be the case, at the EUREX Plant, therefore would avoid the production of 576 drums/year of conditioned secondary wastes as seen before, with cost savings of 416,000 $/y. In the same way the cost savings for the application to the vitrification plant in the case of the solidification of EUREX HLW, avoiding the additional production of 500 drums, would be 362,000 $/year.

CONCLUSION

The application of the NO_x catalytic abatement to radioactive wastes conditioning plants in the place of the scrubbing towers appears to be very attractive both from the environmental protection and from the economic point of view. The process, according to the laboratory experience, seems to work easily on condition that the operational parameters are well controlled. The very low salts concentrations in the secondary wastes produced in the process, permit their dilution and discharge, while scrubbing on the contrary produces large amounts of nitrate salts solutions which have to be conditioned at high supplementary costs.

The cost savings, calculated with reference to a bituminization plant and to a pot vitrification plant of the size needed by the Italian Pilot Reprocessing Plant EUREX, referring to the year 1980 prices, would be 416,000 and 362,000 $/year respectively.

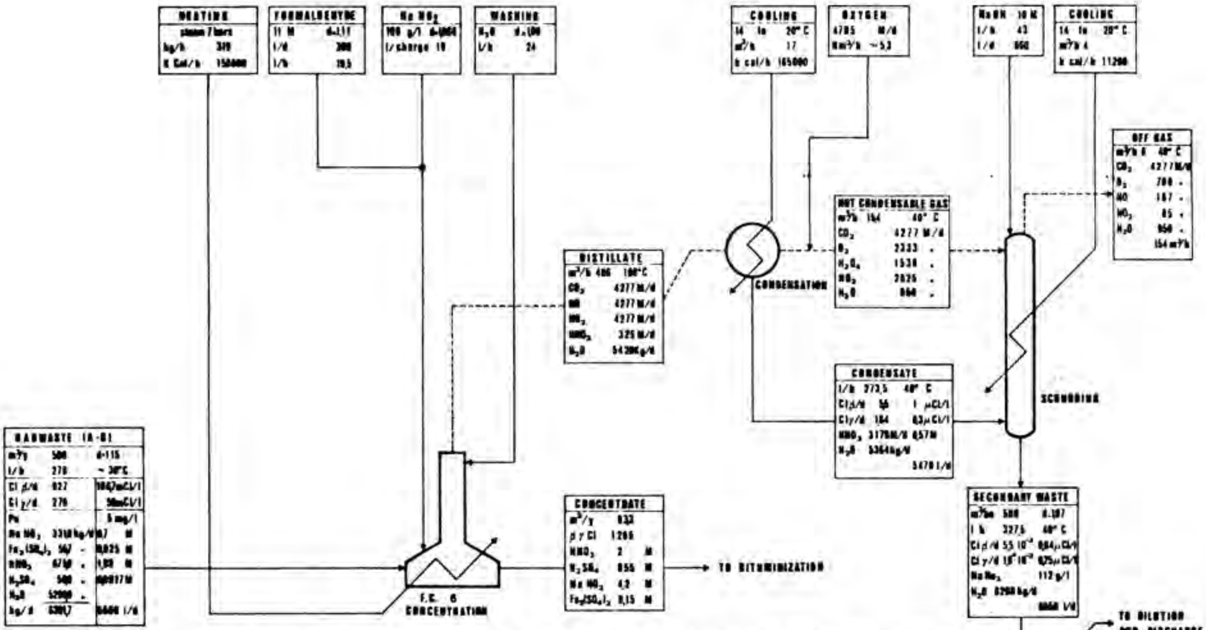

FIG. 1 FLOW SHEET OF THE PRETREATMENT OF M.L. WASTE BEFORE BITUMINIZATION WITH NO_x ALKALINE SCRUBBING

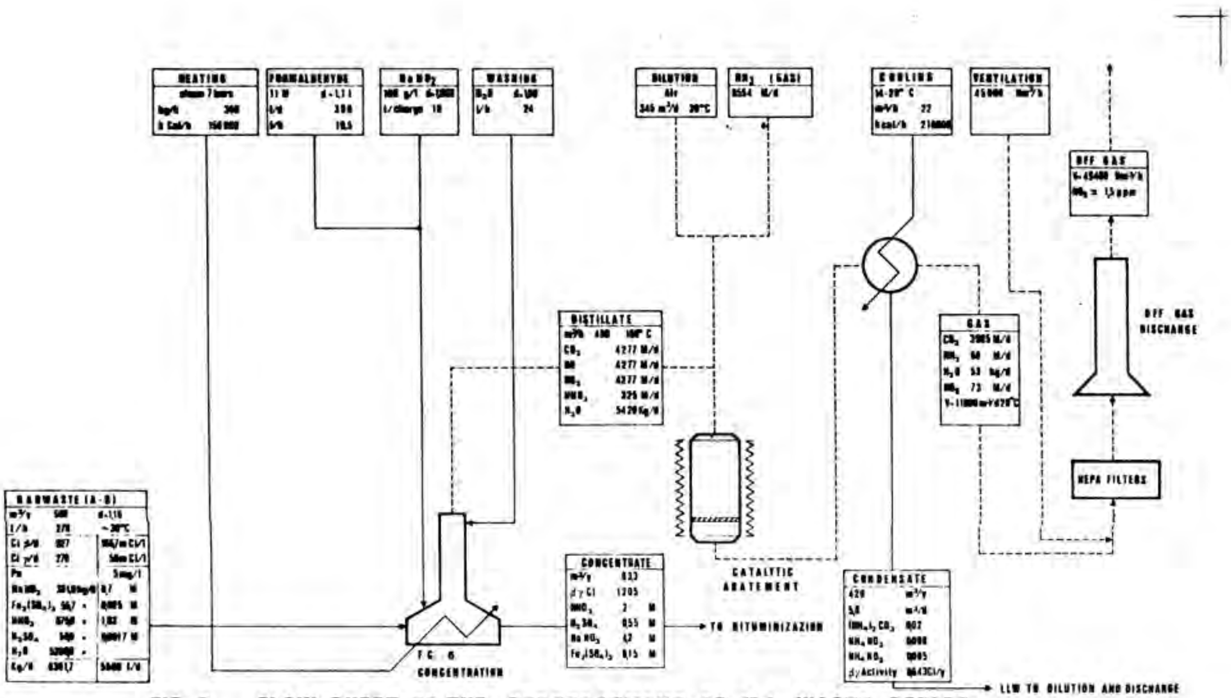

FIG. 2 FLOW SHEET OF THE PRETREATMENT OF M.L. WASTE BEFORE BITUMINIZATION WITH NO_x CATALYTIC ABATEMENT

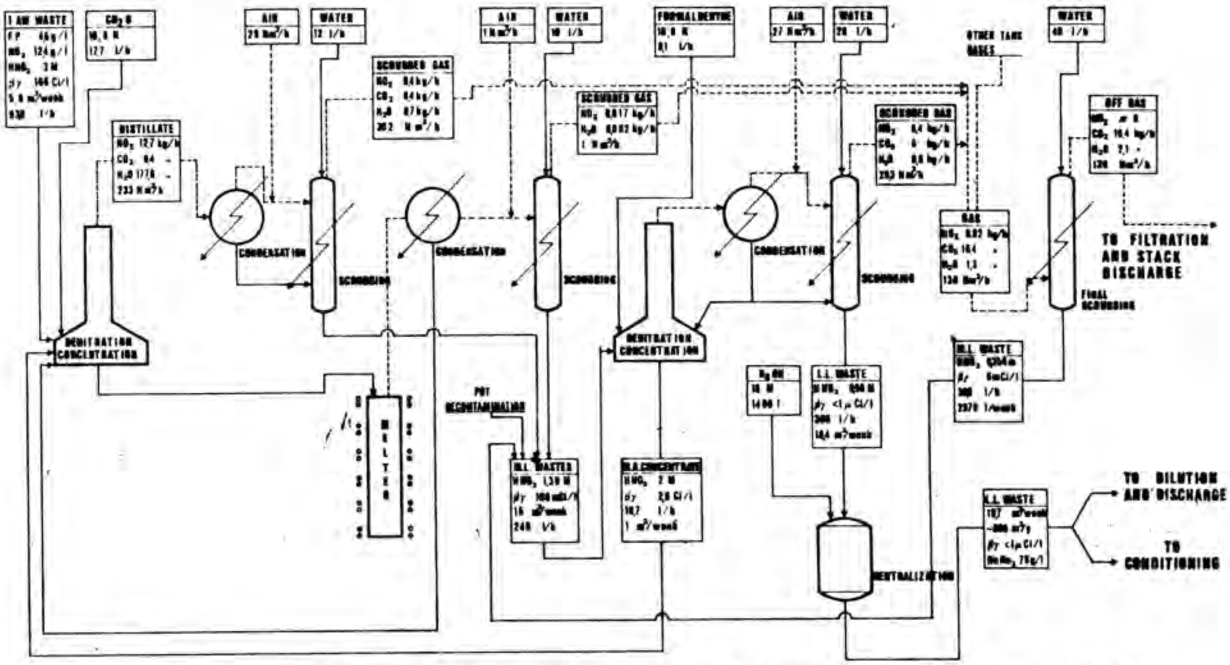

FIG. 3 SIMPLIFIED FLOW SHEET OF THE IVET VITRIFICATION PROCESS FOR H.L.W. SOLIDIFICATION

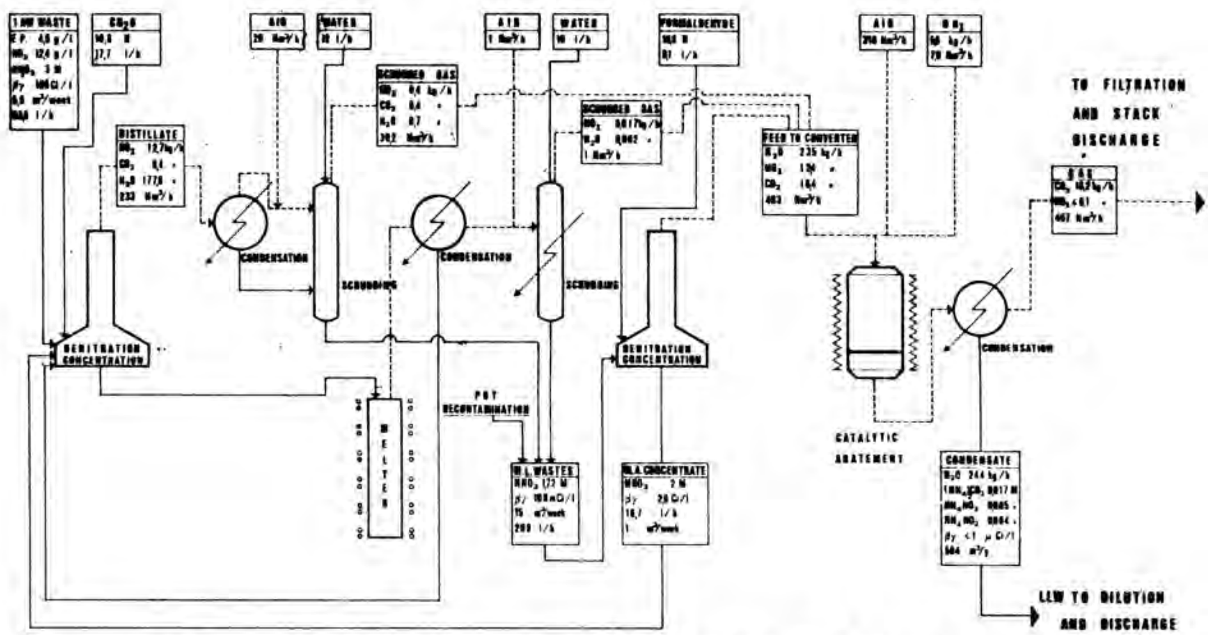

FIG. 4 SIMPLIFIED FLOW SHEET OF THE IVET VITRIFICATION PROCESS FOR H.L.W. SOLIDIFICATION WITH NO_x CATALYTIC ABATEMENT

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