



78

STRATEGY AND CURRENT STATE OF RESEARCH ON ENHANCED IODINE SEPARATION DURING SPENT FUEL REPROCESSING BY THE PUREX PROCESS

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ABSTRACT

An enhanced separation process designed to recover and purify molecular iodine desorbed during dissolution is described in the context of ^{129}I management in the PUREX process for transmutation or interim storage. It involves reducing acid scrubbing with hydroxylammonium nitrate followed by oxidation with hydrogen peroxide to obtain selective desorption. The stoichiometry and kinetics are determined for each step and an experimental validation program is now in progress using a small pilot facility equipped with a scrubbing column. The technical feasibility of the process has already been demonstrated : room-temperature scrubbing with a HAN solution ($0.5 \text{ mol}\cdot\text{L}^{-1}$) at a pH of about 5 results in 99% iodine trapping efficiency ; the subsequent desorption yield is 99.5%.

Keywords: hydroxylammonium nitrate, nitrogen oxides, iodine, hydrogen peroxide, dissolution off-gas treatment

1 - INTRODUCTION

Iodine is one of the most abundant fission products in spent nuclear fuel. Once the short-lived isotopes have disappeared, ^{129}I accounts for about 80% of the residual iodine mass, with the remainder being the stable isotope. With a half-life of 15.7 million years, ^{129}I is one of the main long-lived fission products (LLFP) because its high mobility in the natural environment can lead to a potential radiotoxicity hazard after more than a few thousand years, even if it remains minor in comparison with the actinides. Sea discharge (isotopic dilution), is the currently approved management route after separation during spent fuel reprocessing. Within the framework of the French law passed in 1991 about long lived nuclear waste management, other disposal options for ^{129}I currently being investigated by the CEA, include transmutation or conditioning in a suitable matrix for interim storage or final disposal. The aim of the research programme reported here, is to separate and purify the iodine in a reprocessing plant in order to meet the requirements of these options.

The proposed process originated with an approach and a preliminary study presented at an earlier session of this conference [1]. The experimental work undertaken to acquire the basic scientific knowledge necessary for development of the process is briefly reviewed, followed by a summary of the initial tests results obtained in a small pilot unit.

2 - ASSESSMENT AND PROPOSED SEPARATION PROCESS

Iodine recovery today is based mainly on the PUREX process. When spent UOX fuel is dissolved in hot nitric acid, most of the caesium iodide is oxidized into volatile molecular iodine, I_2 , which, under suitable process conditions, desorbs as a gas and is thus separated from the main liquid process stream. About 99% of the molecular iodine in the gas is trapped in a soda scrubbing column; in a final step of the dissolver off-gas treatment, before atmospheric release, the remainder is chemisorbed on iodine filters made of porous mineral support impregnated with silver nitrate (gas stream decontamination factor > 1000). In the French reprocessing plants at La Hague, almost all the iodine initially contained in the spent fuel is concentrated in a single sodium iodide liquid stream and discharged into the sea.

The separation process presented in this paper is designed mainly to recover the gaseous iodine desorbed in the dissolution stage, perform its purification in $\beta\gamma$ -emitters and finally obtain a solid, stable compound compatible with subsequent treatment. This process was conceived to avoid any capital cost supplement for industrial implementation, to remain simple to operate in existing plants, compatible with liquid waste management routes particularly medium and high-level liquid waste vitrification and complying with all safety criteria. It is shown schematically in figure 1 in a configuration in which iodine is submitted to a specific conditioning process in order to allow an interim storage, and for which PbI_2 is a likely candidate at this time.

The process includes three main successive steps relating to iodine :

① Recovery from the dissolution off-gas by reducing scrubbing with hydroxylammonium nitrate (HAN) in an acidic medium (instead of the current alkali medium). In such a solution, HAN reduces molecular iodine to iodide anion and could also react, in some extent, with the nitrous acid obtained by absorbing NO and NO_2 resulting from the nitric dissolution.

② Decontamination in $\beta\gamma$ -emitters by selective desorption following iodide oxidation by adding H_2O_2 to the primary scrubbing solution ; simultaneously, hydrogen peroxide also destroys the excess of HAN.

33 / 41

③ Conversion to a solid and stable form suitable for interim storage pending final disposal route (PbI₂ for instance), after absorption of the gaseous iodine purified previously.

Besides the advantages mentioned above, HAN is a "C,H,O,N" reagent easy to get rid of and, thus, does not increase the saline load of the effluents to be vitrified. Other advantages of the HAN process were also identified, but are not directly related to the results presented here.

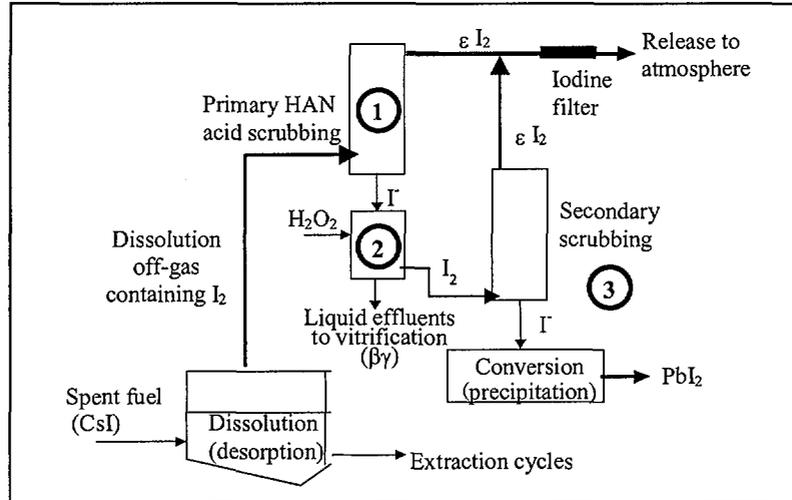


Figure 1 : Schematic of an advanced iodine separation process from dissolution off-gases

Research on the first two steps is currently at an advanced state, as discussed below : after academic studies first carried out in aqueous solution to understand the reaction mechanisms involving iodine (work performed in collaboration with French universities), experiments have been conducted in a small laboratory-scale pilot facility dedicated to gas trapping studies, to confirm the potential of the process with the chosen reducing reagent and to validate the scientific and technical options initially considered for the separation/purification process.

The third step, which will not be discussed here, has already been investigated in previous studies and a reassessment is now under way to ensure that it fits well to the primary HAN acid scrubbing.

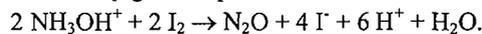
It should be noted that a review of the advantages and disadvantages of the HAN acid process was carried out in comparison with a sodium hydroxide scrubbing process which would be systematically followed by an acidification step using HNO₃ to desorb iodine.

3 - REDUCTION AND OXIDATION OF IODINE, NITROGEN MONOXIDE AND DIOXIDE

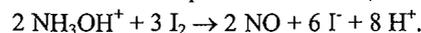
After preliminary feasibility tests confirmed the ability of hydroxylammonium nitrate (HAN) to quickly reduce iodine and nitrous acid in acidic media as well as the hydrogen peroxide one to oxidize iodide anion in the same solution [1], the reactions were investigated in detail ; the main steps and results of this work are described below.

3 - 1 - REDUCTION OF MOLECULAR IODINE BY HAN IN AN ACIDIC AQUEOUS SOLUTION

The lack of former publications about the reaction in acidic solution justified a work which was carried out during a doctoral dissertation [2, 3]. The reaction stoichiometry was first determined. Two limiting equations were identified, depending on whether the system contains excess of HAN or iodine. In the first case, both compounds react mole for mole and the only gaseous product detected is nitrous oxide :

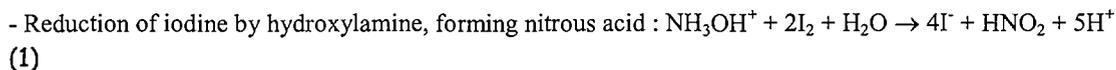


In the second case, 1.5 moles of iodine are consumed per mole of HAN, and the reaction product is nitric oxide :

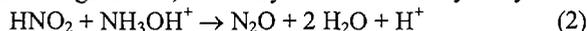


Between these limits, the number of moles of iodine reacting with one mole of hydroxylamine ranges from 1 to 1.5, and both NO and N₂O are produced. Secondly, the study of the reaction to its end-point, using stopped-flow technique together with UV-visible spectrophotometry, led to identify nitrous acid as an intermediate reaction product in every experimental conditions (figure 2). Figure 2-a illustrates the typical evolution of molecular iodine and nitrous acid concentrations with time in most cases. Iodine concentration decreased monotonically, quickly first then more slowly ; however, within a narrow range of initial operating conditions, a nonmonotonic decay of I₂ takes place (figure 2-b). The regeneration of iodine appeared to be promoted by a decrease in both [NH₃OH⁺]/[I₂]₀ ratio, ionic strength and pH; it was also exalted by the addition of iodide to the reactive solution.

Nitrous acid being the only available oxidant, the overall reaction can be split up into three reactions :



- Two possible routes of nitrous acid degradation, either by reaction with hydroxylamine or by reaction with iodide ions :



The monotonic decay in the iodine concentration can be explained as follows. Reduction of iodine (1) is dominating at the beginning of the reaction (figure 2-a, step A); some nitrous acid is formed. Then, reaction (2) becomes predominant (figure 2-a, step B) : $[\text{HNO}_2]$ decreases while iodine keeps on disappearing. When a nonmonotonic decrease in $[\text{I}_2]$ is observed, the onset of the reaction is the same as in the previous case. The regeneration of iodine in the subsequent step can be accounted for by assuming that reaction (3) occurs; iodine accumulates in the reactive medium on condition that its production rate by reaction (3) be greater than its consumption rate by reaction (1). The next step is identical to the B one on figure 2-a.

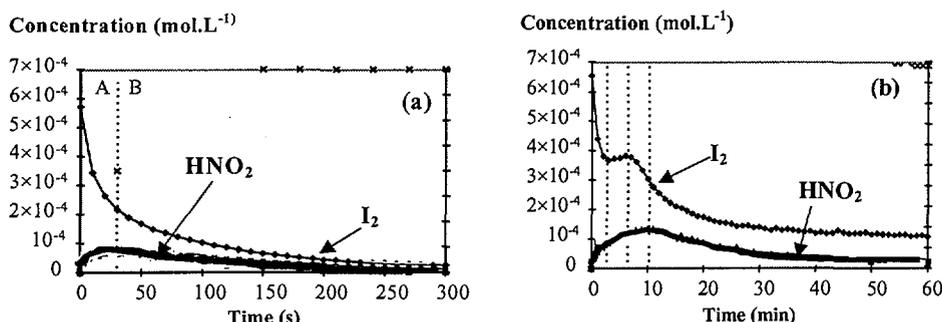


Figure 2 : Concentrations of I_2 and nitrous acid versus time in the iodine-hydroxylamine reaction at $\text{pH}_0 = 1$
 (a) $[\text{I}_2]_0 = 5.5 \times 10^{-4} \text{ mol.L}^{-1}$, $[\text{NH}_3\text{OH}^+]_0 = 3.3 \times 10^{-2} \text{ mol.L}^{-1}$ - (b) $[\text{I}_2]_0 = 6.5 \times 10^{-4} \text{ mol.L}^{-1}$, $[\text{NH}_3\text{OH}^+]_0 = 5.2 \times 10^{-3} \text{ mol.L}^{-1}$

The kinetics of the overall reaction was studied by monitoring the iodine and triiodide concentrations over time. Except where otherwise noted, the results presented below were obtained at 25°C with an ionic strength of 0.5 mol.L^{-1} . The initial rate is directly proportional to the iodine and hydroxylamine concentrations in the reaction medium (first-order reaction). As the pH diminishes, however, the reaction rate decreases. figure 3 shows the values of the pseudo second order rate constant k_0 versus the reciprocal of the initial proton concentration in the medium. Two types of inhibition can be defined, depending on whether the pH is above or below 1.5 :

- At pH values ranging from 1.5 to 3.5, there is a linear relationship between k_0 and $1/[\text{H}^+]_0$: $k_0 = k_1 + k_2/[\text{H}^+]_0$ where $k_1 = 2,20 \pm 0,37 \text{ mol}^{-1}.\text{L}.\text{s}^{-1}$ and $k_2 = 6,64.10^{-2} \pm 0,04.10^{-2} \text{ s}^{-1}$;
- At pH values below 1.5, the relation becomes non-linear : the inflection of the curve reflects the increasing inhibiting effect of the protons.

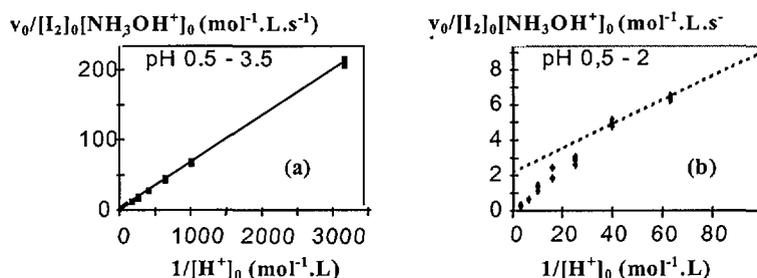


Figure 3: Effect of $[\text{H}^+]$ in the reaction medium on the initial rate of the iodine-hydroxylamine reaction
 (a) $3.10^{-4} \leq [\text{H}^+]_0 \leq 0.3 \text{ mol.L}^{-1}$ ($0.5 \leq \text{pH} \leq 3.5$) - (b) $10^{-2} \leq [\text{H}^+]_0 \leq 0.3 \text{ mol.L}^{-1}$ ($0.5 \leq \text{pH} \leq 2$)

Like protons, iodide ions have their own pH-dependent inhibiting effect.

Finally, in the pH interval from 0.5 to 3.5, it was established that the initial rate of the iodine-HAN reaction can

be described by the following law :

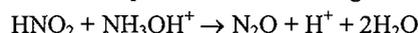
$$v_0 = \left(k_1 + \frac{k_2}{[\text{H}^+]_0} \right) \frac{[\text{I}_2]_0 [\text{NH}_3\text{OH}^+]_0}{1 + k_3 [\text{H}^+]_0 + k_4 [\text{H}^+]_0 [\text{I}^-]_0}$$

where $k_1 = 2,20 \pm 0,37 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$; $k_2 = 6,64 \cdot 10^{-2} \pm 0,04 \cdot 10^{-2} \text{ s}^{-1}$; $k_3 = 10,2 \pm 1,9 \text{ mol}^{-1} \cdot \text{L}$; $k_4 = 42620 \pm 37660 \text{ mol}^{-2} \cdot \text{L}^2$

A mechanism was proposed to account for the experimental results, in which both forms of hydroxylamine NH_2OH and NH_3OH^+ ($\text{pK}_a \sim 6$) are considered to be reactive, and are involved in two symmetrical reaction paths. Nitrous acid, which has been identified as a transient reaction product, could result from the reaction between iodine and nitroxyl, the latter deriving from the decomposition of the intermediate reaction products INHOH and INH_2OH^+ : $\text{HNO} + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + 2 \text{I}^- + 2 \text{H}^+$. Applying the quasi steady-state approximation to the intermediate products INHOH , INH_2OH^+ , HNO and H_2OI^+ leads to the experimental rate law mentioned above. It appears that the unprotonated form of hydroxylamine is the most reactive ($k_{\text{NH}_2\text{OH}}/K_{\text{NH}_3\text{OH}^+} > 25000$).

3 - 2 - REDUCTION BY HAN OF NITROUS ACID AND ABSORBED NITROGEN OXIDES

The reduction of nitrous acid by HAN corresponds to the following overall equation :



This nitrosation reaction occurs only in acidic media; it produces mainly nitrous oxide with traces of hyponitrous acid. Numerous tests were conducted in the pH range between 2 and 4, which had not previously been widely investigated. The initial reaction order with respect to nitrous acid and hydroxylamine was determined for various acidity values. At high acidity (pH = 0.5 and 1.7), the reaction is a first-order with respect to the two reagents but, when the proton concentration diminished, the reaction order increased towards 2 for nitrous acid and decreased towards 0 for hydroxylamine. The effect of the proton concentration in the medium on the second-order kinetic constant clearly revealed two domains : when $\text{pH} < 1.7$, an affine relationship exists between k_0 and $[\text{H}^+]_0$ (N-nitrosation by H_2NO_2^+ made easier), while, for less acidic solutions, the curve is inflected (N-nitrosation by N_2O_3 made easier). Nevertheless, an empirical rate law was established for the complete pH range investigated :

$$v_0 = x \left\{ k_1 [\text{HNO}_2]_0 [\text{NH}_3\text{OH}^+]_0 [\text{H}^+]_0 + k_2 [\text{HNO}_2]_0 [\text{NH}_3\text{OH}^+]_0 \right\} + (1-x) \left\{ \frac{k_3 [\text{HNO}_2]_0^2 [\text{NH}_2\text{OH}]_0}{k_4 + [\text{NH}_2\text{OH}]_0} \right\}$$

where $x = [\text{HNO}_2]/[\text{HNO}_2]_{\text{tot}}$ and $1-x = [\text{NO}_2^-]/[\text{HNO}_2]_{\text{tot}}$

$k_1 = 3,00 \pm 0,15 \text{ mol}^{-2} \cdot \text{L}^2 \cdot \text{s}^{-1}$; $k_2 = 0,30 \pm 0,03 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$; $k_3 = 0,84 \pm 0,02 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$; $k_4 = (1,3 \pm 0,1) \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

This study also revealed the strong catalytic power of iodide ions. The experiments had to be performed in a weak acid medium ($\text{pH} > 2.5$) to avoid any undesirable reaction between iodide ions and nitrous acid catalyzed by the protons: $2\text{HNO}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{NO} + 2\text{H}_2\text{O}$. Adding iodide ions ($4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) to the reaction medium containing hydroxylamine ($10^{-2} \text{ mol} \cdot \text{L}^{-1}$), nitrous acid ($5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$), and protons ($4,47 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) multiplied the reaction rate by 10. Consider the contribution (designated v_1) of catalysis by iodide ions to the overall reaction rate : v_1 is proportional to $[\text{I}^-]_0$, $[\text{NH}_3\text{OH}^+]_0$ and $[\text{HNO}_2]_0$. On the other hand, variance analysis of the series of test results obtained by varying the acidity showed (within a 95% confidence interval) that v_1 is independent of $[\text{H}^+]_0$. Thus $v_1 = k_5 [\text{HNO}_2]_0 [\text{NH}_3\text{OH}^+]_0 [\text{I}^-]_0$, where $k_5 = 8600 \pm 750 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$; this corrective term, to be added to the expression of the rate v_0 mentioned above, is typical of a N-nitrosation of NH_2OH by NOI .

Finally, the NO/NO_2 /hydroxylamine reaction system was studied in solution at $\text{pH} < 5$. When nitrogen dioxide was not present, the monoxide form was not absorbed in solution but in the presence of NO_2 , two outcomes were possible depending on the $[\text{NO}_2]_0/[\text{NO}]_0$ ratio :

- When the ratio was less than 0.2, the gas phase at the end of the reaction contained both nitrous and nitric oxide, but all the nitrogen dioxide had reacted. The solution contained neither nitrite nor nitrate ions. As many moles of NO were consumed as moles of NO_2 .
- Two significant differences were observed when the ratio was greater than 0.2 : nitrate ions were detected in solution, and less than one mole of NO was consumed per mole of NO_2 ; the NO/NO_2 consumption ratio decreased as the $[\text{NO}_2]_0/[\text{NO}]_0$ ratio increased.

The solution pH and the initial hydroxylamine concentration had no significant effect on the nature and concentration of the reaction products. Nitrogen monoxide was reduced to nitrous oxide by hydroxylamine, but with very slow reaction kinetics.

The observed results can be interpreted by postulating an absorption mechanism in acidic media (figure 4), together with reduction of the nitrous acid to nitrous oxide by hydroxylamine: $\text{HNO}_2 + \text{NH}_3\text{OH}^+ \rightarrow \text{N}_2\text{O} + \text{H}^+ + 2\text{H}_2\text{O}$. Two parallel reaction paths can be considered :

- A : Absorption of NO_2 and N_2O_4 in solution and hydrolysis of N_2O_4 forming nitrous and nitric acids.
- B : Absorption NO , NO_2 and N_2O_3 in solution and hydrolysis of N_2O_3 forming nitrous acid.

The experimental results indicate that mechanism A is negligible when the $[\text{NO}_2]_0/[\text{NO}]_0$ ratio is less than 0.2.

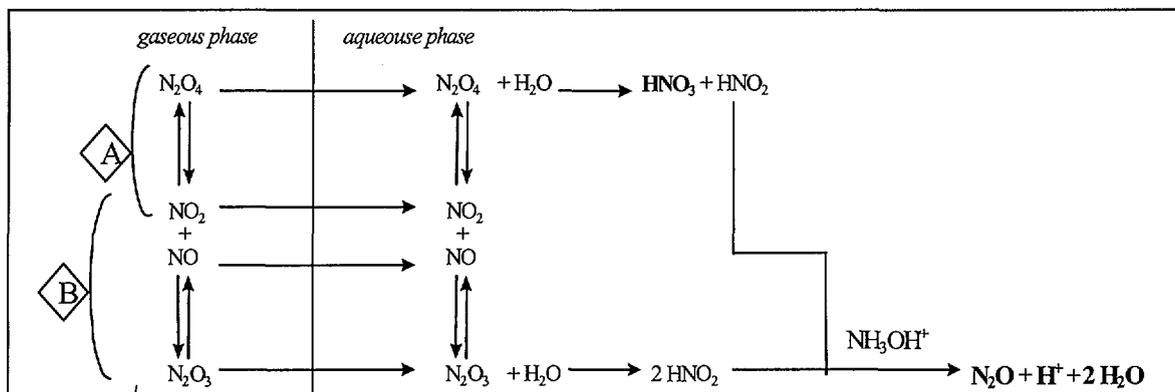


Figure 4 : Absorption mechanism for an NO/NO₂ gaseous mixture in an acidic hydroxylamine solution

3 - 3 - MODELING THE I₂/I⁻/HNO₂/NH₃OH⁺/H⁺ SYSTEM

Of the many reactions in solution that could possibly occur during scrubbing of the dissolution off-gas stream by a HAN solution, three major reactions can be identified in acidic media: reduction of iodine and nitrous acid by hydroxylamine, and oxidation of iodide ions by nitrous acid.

Two models can be proposed for the I₂/I⁻/HNO₂/NH₃OH⁺/H⁺ system. The first is based on the rate laws for these three reactions, and satisfactorily accounts for the experimental results at 25°C and at pH 2 or higher, thus substantiating the kinetic laws established experimentally under these conditions for the I₂/NH₃OH⁺ and HNO₂/NH₃OH⁺ reactions. The restricted validity range of this model limits its usefulness, however. The second is an empirical model with a broader experimental basis. It postulates a second-degree polynomial relation for which the coefficients were estimated from two optimized experimental matrices : one consisting of a classic Doehrlert network, and the other constructed using the Fedorov algorithm. This model was used to determine favorable conditions for rapid reduction of 95% of the iodine and nitrous acid during the solution residence time in the column, i.e. about 8 seconds. Considering the economic constraints, which require the use of the lowest possible scrubbing reagent concentration and operation near room temperature, a satisfactory and relatively robust operating point can be obtained at a pH near 2, and a temperature of 25°C with a 15-fold excess of hydroxylamine relative to nitrous acid, provided the [HNO₂]₀/[I₂]₀ ratio exceeds 150.

This work was done in a closed reactor in which all the reagents were added directly in solution. Although the kinetics obtained are not immediately transposable to the process, they do confirm that hydroxylamine rapidly and simultaneously reduces iodine and nitrous acid under acceptable concentration, acidity and temperature conditions, and demonstrate the feasibility of the process. Further work was carried out with an experimental configuration more representative of the process, with absorption of the gaseous nitrogen oxides and iodine in a continuously-fed reactor with recycling.

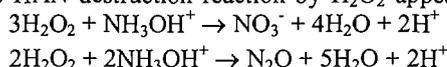
3 - 4 - IODINE DESORPTION BY HYDROGEN PEROXIDE

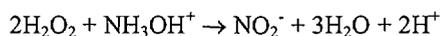
The oxidation of iodide ions by hydrogen peroxide produces molecular iodine quantitatively if pH is less than 2 : $2\text{I}^- + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$.

Although the oxidation of iodide to iodate by hydrogen peroxide is thermodynamically possible, the process is complex and has not been fully elucidated ; only the stoichiometry has been firmly established at the present time : $\text{I}_2 + 5\text{H}_2\text{O}_2 \leftrightarrow 2\text{H}^+ + 2\text{IO}_3^- + 4\text{H}_2\text{O}$. This autocatalytic reaction does not occur in the absence of iodate, nor at low acidity (pH > 2.4). Increasing the pH shortens the induction time, which nevertheless remains long in the absence of iodate : 8 hours if pH = 0.05, and 8 to 11 days when pH = 2.4 (for [H₂O₂]₀ = 5 × 10⁻³ mol.L⁻¹ and [I₂]₀ = 5 × 10⁻⁴ mol.L⁻¹). Iodine reduction by H₂O₂ ($\text{I}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{I}^- + \text{O}_2 + 2\text{H}^+$) can occur when pH > 2. At a pH higher than 6, the oxidation of iodide to iodine by H₂O₂ is followed by the reduction of iodine to iodide by reducing H₂O₂, and the H₂O₂ decomposition overall reaction is observed, catalyzed by the I₂/I⁻ couple.

The experimental work confirmed that within the pH range of the off-gas scrubbing solution using HAN (i.e. 2 to 4), the oxidation of iodide by H₂O₂ does not progress beyond molecular iodine, and that the kinetics are reproducible. Conversely, in the case of the oxidation of iodide ions by nitric acid, with poor reproducibility due to the catalysis by nitrous acid, the reaction could continue until the iodine was at oxidation state +1 (H₂OI⁺).

On another hand, the stoichiometry of the HAN destruction reaction by H₂O₂ appears to be complex, with a balance involving three reactions :





However, the oxidation of hydroxylamine to nitrate and nitrous oxide predominates, and the production of nitrite ions has never been observed to exceed 1% of the HAN present in the solution.

This work continues with a study of the catalysis of this reaction by iodide ions.

4 - PILOT-SCALE EXPERIMENTS

A small pilot unit was built to confirm the potential results previously determined in the laboratory and to validate the initial scientific and technical options under conditions more representative of a possible industrial operation (continuously-fed reactor including gas-liquid transfer). The following results concern mainly the first step in the separation process — iodine recovery by acid scrubbing with HAN — and, to a lesser extent, iodine desorption by H_2O_2 .

4.1. DESCRIPTION

The pilot facility used for this study (called MALAGA i.e. Module d'Analyse et de Lavage des Gaz) included a counterflow packed column (50 mm I.D. \times 1 m high) in which the gas stream containing iodine was scrubbed by a HAN solution (figure 5). The off-gas flow to be treated ($Q_{\text{air}} = 2000 \text{ NI.h}^{-1}$; $[\text{NO}] + [\text{NO}_2] = 2400 \text{ vpm}$, $[\text{NO}_2]/[\text{NO}] = 0.25$; $[\text{I}_2] = 7 \text{ vpm}$) is reconstituted directly in the facility (NO and NO_2 supplied by gas cylinders; I_2 produced by the Dushman reaction in sulphuric medium) just before entering the packed column, and then flows through a bubble column filled with sodium hydroxide; the HAN solution circulates in a closed loop, implying that iodide accumulates in solution.

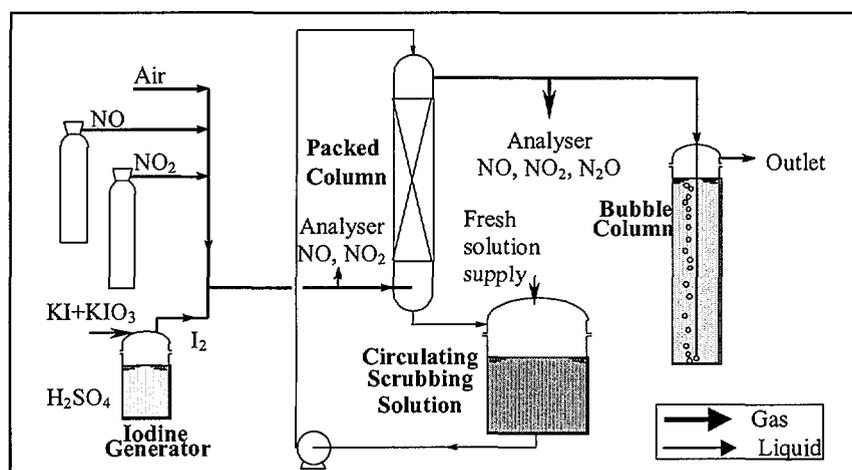


Figure 5 : Pilot facility schematic

The nitrogen oxides concentrations in the gas phase are continuously monitored in the column inflow (NO, NO_2) and outflow (NO, NO_2 , N_2O) lines. The iodide, nitrite and nitrate ions concentrations are monitored by sampling the circulating scrubbing solution at regular intervals (according to experimental conditions : ion selective electrode or ICP or UV spectrophotometry for I; UV spectrophotometry or ion chromatography for NO_2^- and NO_3^-).

4.2. IODINE RECOVERY BY ACID HAN SCRUBBING

The iodine recovery efficiency (R%) is estimated from the quantity of iodine measured in the soda solution (bubble column) and the one supplied by the initial reagents:

$$R\% = 100 \times [1 - (\text{quantity of iodine trapped in the soda solution} / \text{quantity of iodine entering the system})].$$

Unlike the laboratory tests, the pilot facility does not allow to control the nitrous acid concentration in the scrubbing solution independently of the other parameters. The molecular iodine concentration in the gas stream being representative of actual plant conditions and, consequently, kept constant throughout the first pilot-scale tests, the chemical parameters considered for an estimation of their effect, are thus the pH and the HAN concentration, which can be maintained constant throughout the duration of one experiment by supplying fresh solution of suitable reagents.

- Experiments without either NO or NO_2 in the scrubbed gas :

The tests carried out with a gas flow stream containing no nitrogen oxides, with a 0.05 M HAN solution, and without regulating the pH, showed that iodine can be trapped with $98\% \pm 1\%$ efficiency within the pH range from 3.0 to 4.5.

• Experiments with NO and NO₂ in the scrubbed gas :

Figures 6-a and 6-b illustrate the results of tests with nitrogen oxides ([NO]+[NO₂] = 2400 vpm, [NO₂]/[NO] = 0.25) and without regulation of the solution pH. Figure 6-a shows that the quantity of iodine in solution diminishes over time in comparison with the quantity of iodine (expressed as iodide equivalent) injected in the column ; this reflects a major drop in the recovery performance, together with a drop in the pH because of the formation of protons following the absorption of NO and NO₂ and the reduction of nitrous acid, their hydrolysis product, by HAN. Figure 6-b corresponds to a test that was initially identical with the test in Figure 6-a, but during which the nitrogen oxide concentration was diminished by a factor of 25 after 1.5 h ; this had an immediate effect on the iodine behavior : the iodine concentration profile in solution, versus time, became parallel with the injected iodine profile (97% efficiency) despite the low pH.

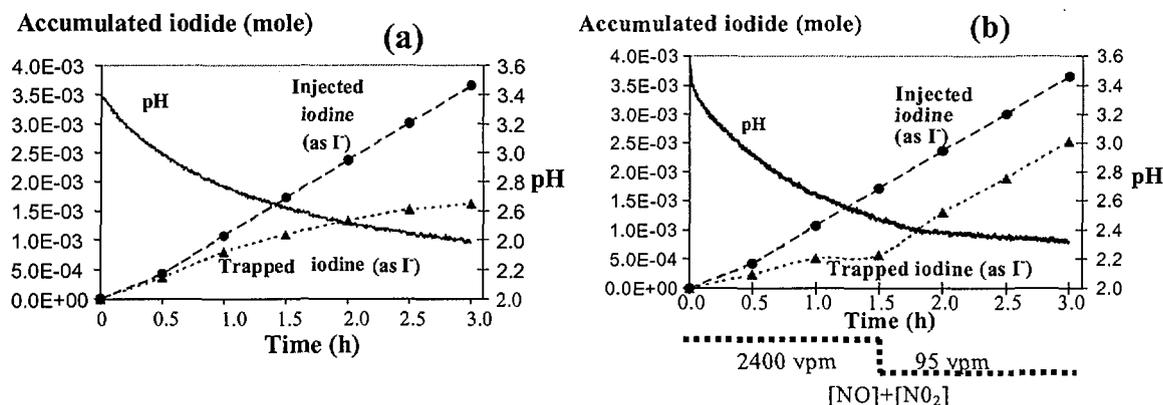


Figure 6 : Effect of nitrogen oxides on iodine recovery efficiency

($Q_{air} = 2000 \text{ NL.h}^{-1}$; $[I_2] = 7 \text{ vpm}$; $[NO]+[NO_2] = 2400 \text{ vpm}$; $[NO_2]/[NO] = 0.25$; $[NHA] = 0,5 \text{ M}$; $T = 25^\circ\text{C}$)

Thus, these two experiments reveal that the iodine trapping performance is increasingly sensitive to the solution pH when nitrogen oxides are present in the system. This phenomenon could be explained by iodine regeneration due to the oxidation of iodide by nitrous acid, made easier when pH decreases : $2 \text{ HNO}_2 + 2 \text{ I}^- + 2 \text{ H}^+ \rightarrow \text{I}_2 + 2 \text{ NO} + 2 \text{ H}_2\text{O}$. During the reduction of I₂ by HAN in closed reactor (cf. section 3), this reaction was considered as a possible secondary route of nitrous acid degradation to account for the nonmonotonic decrease of iodine concentration observed in some experimental conditions. Its rate increases and it becomes predominant when nitrous acid accumulates in the solution (degradation kinetics of the same order of magnitude as the supply through NO and NO₂ absorption) as well as the protons resulting from its reduction by HAN ; given the large excess of HNO₂ in respect to iodine because, by far, of the absorption of NO and NO₂ instead of being an intermediate product resulting from the reduction of I₂, the assumption that iodide ions are thus oxidised in conditions rather different from those observed in laboratory scale (particularly for the pH) is credible.

Under these conditions, increasing the HAN concentration (from 0.05 M to 0.5 M) had no effect.

Tests conducted at various regulated pH values with a HAN concentration of 0.5 M in solution confirmed the effect of the pH (Figure 7) on the iodine trapping efficiency, and the observed profile is consistent with the previously proposed rate law (cf. section 3). The presence of nitrogen oxides thus requires the use of a solution with a pH of about 5 to obtain 99% efficiency. The absorption efficiency of nitrogen oxides remains constant in the range of 15 to 20 % whatever the solution pH, and the products are nitric and nitrous acids. Conversely, the rate at which nitrous acid is destroyed by HAN diminishes when pH raises, leading to an accumulation of nitrite ions in solution that can be partially controlled by increasing the solution temperature. However, the main product of the HNO₂-HAN reaction remains nitrous oxide (Table 1), the remainder being nitrate ions resulting from NO₂ hydrolysis.

| Scrubbing solution pH | 3,5 | 4,5 | 5 | 5,5 |
|---|-------|-----|----|-----|
| N ₂ O produced (% of trapped NO+NO ₂) | 62 | 55 | 52 | 41 |
| NO ₂ ⁻ in solution (% of trapped NO+NO ₂) | < 0,1 | 4 | 20 | 29 |

Table 1 : Effect of the pH on the reaction products distribution during scrubbing of a NO + NO₂ containing air stream by HAN

Tests are now in progress to study more precisely the pH effect in the range 4,5 - 5,5 as well as the NO and NO₂ concentrations ones, in the gas stream ; then, the operating parameters will be optimized to improve the performance of the scrubbing step.

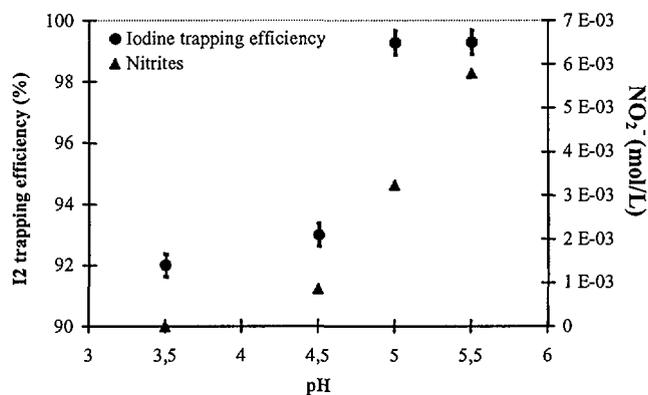


Figure 7 : Effect of pH on iodine trapping efficiency in the presence of nitrogen oxides and on final nitrite ion concentration measured in the scrubbing solution ($Q_{air} = 2000 \text{ Nl.h}^{-1}$; $[I_2] = 7 \text{ vpm}$; $[NO] + [NO_2] = 2400 \text{ vpm}$; $[NO_2]/[NO] = 0.25$; $[NHA] = 0,5 \text{ M}$; $T = 25^\circ\text{C}$)

4.3. IODINE DESORPTION AND DESTRUCTION OF EXCESS HAN BY THE ADDITION OF H₂O₂

Unlike the scrubbing step, the desorption conditions in the MALAGA facility are the same as the laboratory ones and specific tests at pilot scale level are not really useful except for validation. For the moment only one experiment was performed in MALAGA with a synthetic scrubbing solution ($[NHA] = 0.05 \text{ mol.L}^{-1}$; $[I] = 0.002 \text{ mol.L}^{-1}$). An addition of H₂O₂ at room temperature, leads to a total destruction of HAN and to an iodine recovery after desorption, over 99.5 %.

Additional laboratory tests will address the nitrite ion effect on iodide oxidation when HAN is present.

5 - CONCLUSION

In the course of research on management routes for LLFP, a separation and purification process was proposed for the iodine found in the PUREX process dissolution off-gas stream. It includes three steps:

- iodine recovery from the dissolution off-gases by reducing scrubbing with hydroxylammonium nitrate (HAN) in an acidic medium;
- iodine decontamination of $\beta\gamma$ -emitters through selective desorption of I₂ by hydrogen peroxide, which also simultaneously destroys the excess of HAN;
- iodine conversion to a solid and stable form suitable for interim storage pending final disposal (which is outside the scope of this article).

Academic studies in solution (closed reactor), led to determine an optimal compromise at a value of about 2, for the pH which has antagonistic effects on the iodine and nitrous acid reductions. The iodine recovery step was validated in a small laboratory pilot unit. Scrubbing by a HAN solution at room temperature yielded 99% iodine trapping efficiency if pH is raised up to 5. Under these conditions, the nitrogen oxides were partially absorbed and nitrite ions were observed to accumulate in solution. The results show a major difference between closed reactor experiments and tests in a continuously-fed scrubbing column (gas-liquid transfer) with solution recycling.

Tests showed that 99.5% iodine desorption efficiency can easily be obtained from the HAN scrubbing solution by adding hydrogen peroxide. The nitrite ions in solution are oxidized to nitrates by hydrogen peroxide, preventing the formation of NO and NO₂ that could hinder the subsequent conversion step.

The experimental program now in progress seeks to optimize the process operating parameters.

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