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Distillation of radioactive liquid organic wastes for subsequent wet oxidation

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Abstract

The nuclear industry has considerably contributed to the development of methods and procedures to cope with and solve the problems of safety and management of hazards. One of the problems of spent nuclear fuel reprocessing management is the treatment of organic radioactive wastes. This paper is intended to present a new process for radioactive waste treatment, based on two combined steps, i.e. preliminary distillation and wet oxidation. The results of distillation tests, carried out in a laboratory scale apparatus, on both simulated and radioactive liquid solutions, are reported. The tests carried out with simulated solution prove to be of significant value for a more thorough and fundamental understanding of distillation equipment. High decontamination factors were obtained by distillation of radioactive waste, showing no need for further particular treatment of the distillate. A noteworthy result from the point of view of safety and management of hazards connected to radioactive wastes in nuclear plants is the remarkable reduction in the volume of contaminated liquid wastes, which should encourage further investigations with a view to utilizing industrial distillation plant. © 1998 Elsevier Science B.V.

Keywords: Radioactive waste; Solvent distillation; Wet oxidation

1. Introduction

In the field of safety and management of hazards, the nuclear industry has played a very important role in defining methods and procedures.

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One remarkable problem, even if not of primary importance, concerns reprocessing of spent fuel elements.

Spent solvent management is a minor problem of the nuclear fuel cycle, because of the low degree of radioactivity of this liquid waste. Nevertheless a reliable standardized technology has not so far been worked out, which may be universally considered as reference treatment and conditioning process for this kind of waste.

Although incineration is the most obvious method to be applied for the conditioning of radioactive organic waste, alternative treatment options, mainly chemical processes, for spent solvent (usually tri-butyl phosphate (TBP) in odourless kerosene) [1] are being investigated.

In fact the sophisticated and expensive technology needed for incineration may be justified only by large quantities of waste to be treated, possibly together with other kinds of incinerable radioactive waste (e.g., solid waste). Public acceptability of an incineration plant for radioactive waste is also to be considered in the decision-making process.

The criteria for solvent treatment process may be summed up as follows [2]:
· reasonable chance of successful development on an acceptable timescale, proved at pilot scale with active species;
· demonstrated to be safe with little uncertainty and compatible with associated plant;
· simple, easy to control process. Minimum process steps/unit operations;
· demonstrated acceptable lifetime costs.

Taking into account the above consideration, alternative treatment options, mainly chemical processes for spent solvent, were considered in the past and are being investigated at present. Some examples are briefly described below:

The process proposed for Sellafield consists of: an initial multi-stage solvent wash, a central alkaline hydrolysis treatment process, combustion of the residual organic material, conditioning of the aqueous reaction products to ensure compatibility with downstream plants [2].

The Eurowatt Process has been developed by Belgian Eurochemic. It consists in the extraction of TBP, degradation products and radionuclides from spent solvent mixtures by anhydrous phosphoric acid, followed by the pyrolysis of the radioactive TBP–phosphoric acid phase at about 200°C, in order to decompose the organic compounds, transforming them into volatile hydrocarbons, to be burned, and non-volatile inorganic phosphoric acid solution, containing all the activity, to be solidified [3].

Immobilization in Portland cement with the use of emulsifiers and other additives has been realized by the Hanford Engineering Development Laboratory (USA), because incineration was found too costly for the small amount of liquid organic waste to be treated yearly [4].

Electrochemical oxidation is under development at Dounreay (UK) AEA Tecnology site (Silver II Process). The process is based on the oxidation of the organic matter by means of highly-reactive species of silver ions (Ag^{2+}) generated by electrical supply at the anode of an electrochemical cell, at low temperature and pressure [5].

Wet oxidation by means of hydrogen peroxide, in the presence of a catalyst (usually Cu, Fe ions) has been studied by different researchers [6]. As for the electrochemical

oxidation, the main advantages of this process are its mild reaction conditions, e.g., atmospheric pressure and temperature up to 100°C.

Besides the above described processes, the evaporation technique is another considered option in concentrating the volume of the liquid waste and separating the low active distillate [7]. In particular Wiped Film Evaporator has been found to be effective in terms of decontamination factor, reliability and corrosion problems [8].

In Italy, as a result of past reprocessing experimental campaigns, performed at the ENEA EUREX reprocessing pilot plant (Saluggia), about 25 m³ of spent solvent were produced, consisting of a mixture of extractans (TBP and TCA, tri-capryl-amine) and diluents (kerosene and several alkyl-benzenes).

The technique of reprocessing liquid organic waste products having high rates of radioactivity involves problems of storage and disposing. In this kind of management of hazards, the quantities and volumes of waste products obtained are carefully considered.

A problem of remarkable interest to be faced consists in the possibility of reducing considerably the volumes concerned. Hazardous waste minimization according to US EPA [9] is a means for reducing environmental problems caused by the generation, treatment and disposal of hazardous wastes. It is defined as any source reduction or recycling activity that results in either reduction of total volume of hazardous waste, or reduction of toxicity of hazardous waste, or both, as long as that reduction is consistent with the general goal of minimising present and future threats to human health and the environment [10]. The strategy of separating low-level and high- level wastes during pretreatment, by means of proven separation technologies, has been planned in a long-term programme of disposing hazardous radioactive wastes [11].

Taking into account the above considerations, research has been carried out in order to investigate a management scheme based on preliminary distillation followed by wet oxidation of the bottom product.

The expected decontamination factor for the top product should allow conventional incineration without containment.

The distillation technique permits the separation of the feed into two fractions: a 'light' one, consisting essentially of kerosene and alkyl-benzenes, which are not contaminated; a 'heavy' one, consisting of TCA and TBP, containing practically all the radioactivity.

The total envisaged research programme includes the following stages:
1. laboratory distillation tests both with simulated and genuine waste solutions;
2. wet oxidation tests with hydrogen peroxide as oxidising agent.

The aim of the distillation is the separation of the kerosene, which is almost unreactive with hydrogen peroxide, and the reduction of the waste volume to be treated by wet oxidation.

The purpose of wet oxidation is the 'transformation', under mild operative conditions in terms of temperature and pressure, of the spent organic material into inorganic substances as aqueous solutions; in fact, the oxidative decomposition of TBP and TCA produces mainly carbon dioxide, water, phosphoric acid and nitric acid.

The purpose of the present paper is to present a detailed description of the experimental distillation tests.

2. Theoretical assessment

The laboratory scale distillation column has been designed with reference to the following hypotheses [12]:
- ideal mixture (validity of Dalton and Raoult laws).
- assimilation of the heavy fraction (TBP + TCA = about 10% v/v) to TBP only, which is the lowest boiling component.
- assimilation of the light fraction (mesitylene + kerosene + solvesso = about 90% v/v) to n-dodecane, which is the highest boiling component.

On the basis of these hypotheses, we can assume we are working with a binary mixture consisting of the key components TBP(= 10% volume) and n-dodecane(= 90% volume) as molar fractions: $X_{TBP} = 0.085$; $X_{nd} = 0.915$

The distillation equipment has been designed in accordance with the well known McCabe–Thiele procedure [13]. With the hypothesis of constant molar flow rates the operating lines for the rectifying and the stripping section are respectively as follows:

$$Y_{n+1} = \left(\frac{R}{R+1} \right) X_n + \frac{X_D}{R+1} \tag{1}$$

$$Y_{m+1} = \left(\frac{L}{L+B} \right) X_m - B \frac{X_B}{L-B} \tag{2}$$

where L = liquid flow rate in the stripping section, B = bottom flow rate and $R = L/D$ (Reflux ratio).Equilibrium equations are as follows:

$$P_A^0 X_A + P_B^0 (1 - X_A) = P_{tot} \tag{3}$$

$$Y_A = \left(P_A^0 / P_{tot} \right) X_A \tag{4}$$

According to Eqs. (3) and (4), we obtain the liquid–vapor X–Y equilibrium curve of Fig. 1, where the step by step McCabe–Thiele procedure has been performed. Even if the McCabe–Thiele diagram may seem obsolete [14] and, as a design tool, cannot match the accuracy, speed and flexibility of computer simulation, it can provide effective results as a troubleshooting and analytical tool [15].
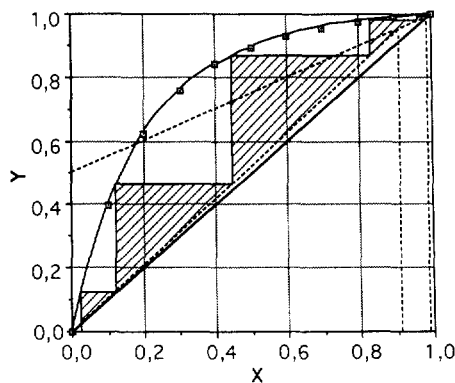

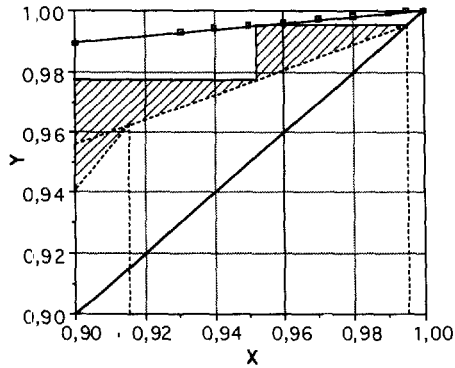Fig. 1. Equilibrium curve TBP/n-dodecane according to McCabe–Thiele procedure.

Fig. 2. Detail of the equilibrium curve TBP/n-dodecane ($X > 90$, $Y > 90$), according to McCabe–Thiele procedure.

The detail of the $X-Y$ equilibrium curve, for both X and $Y > 90$ is shown in Fig. 2.

With $R = 1$, we obtain five ideal plates, with the feeding on the second plate, starting from the top of the distillation column.

Because of the wide difference between the boiling temperatures of the diluents (kerosene, mesitylene) and the extractans (TBP and TCA) we decided to set up a batch distillation, limited to the rectifying section [16,17].

By the same calculation, the $X-Y$ equilibrium curve can be used to calculate the number of ideal plates needed to reach an assigned composition in the reboiler, or conversely the composition in the reboiler reached with an assigned number of ideal plates.

As an example, by means of the operating line (2), we point out the composition $X = 0.2$ that can be reached in the reboiler under the following conditions: 5 ideal plates; $X_D = 0.995$ and $R = 1$.

Finally, in order to decrease the boiling temperature (down to ca. 100°C), we decided to perform steam distillation, adding water into the reboiler.

The $X-Y$ equilibrium curve is modified as shown in Fig. 3.

It must be remembered that for packed column the stage idea is not really correct. It is often convenient to use the Height Equivalent to a Theoretical Plate and equilibrium
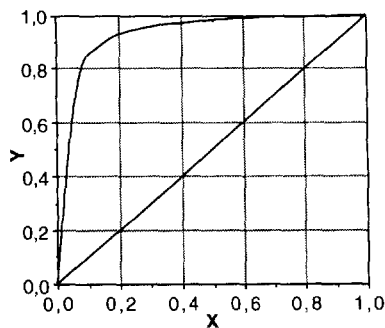

Fig. 3. Steam distillation equilibrium curve.

stages to make simulation, prior to a decision as to whether a column will be packed or trayed [18].

3. Experiment

3.1. Characterization of the waste

Chemical and radiochemical analyses aiming at the complete characterization of the waste, were performed on sampled genuine waste. Analyses were carried out with three replications.

Chemical qualitative and quantitative analyses were carried out by HRGC using a Perkin–Elmer Gas Chromatograph mod. 8700, by the internal standard method.

As shown in Fig. 4, each component of the organic mixture has more than one peak in the gas chromatograph output, except TBP (mesitylene is together with some isomers) because of the use of components which are not absolutely pure . However some peaks have not been identified, probably because of some unknown isomers and/or degradation products. Table 1 shows the main result of the characterization of the waste.
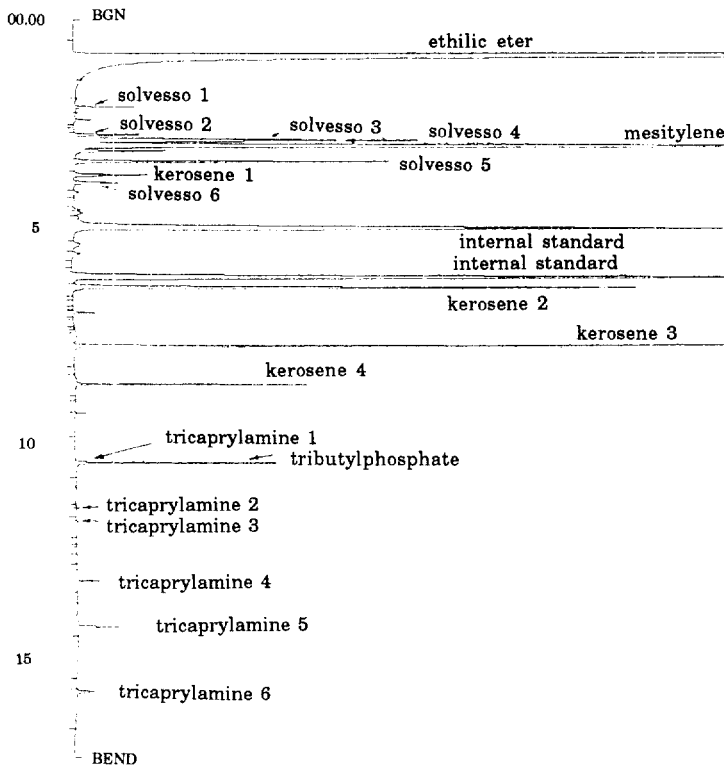

Fig. 4. Gas chromatogram of the organic mixture.

Table 1
Solvent waste main data

Determination	Unit	Value
Density (25°C)	kg l^{-1}	0.810
Mesitylene + solvesso	% v/v	24.8
Kerosene	% v/v	48.6
TBP	% v/v	6.7
TCA	% v/v	4.6
Other	% v/v	15.3
Total α	kBq l^{-1}	52.5
Total β (non volatile)	kBq l^{-1}	175.7
Total β	kBq l^{-1}	900
Total γ	kBg l^{-1}	266

Radiochemical analyses were performed by the following main techniques: The α activity was measured by direct deposition on a cupel, followed by desiccation and calcination (800°C) and measured by a solid scintillation detector (ZnS); The β activity was first measured by direct deposition on a cupel, followed by low temperature desiccation and measured by a solid scintillation detector (anthracene). With this method all the volatile radionuclides (e.g. Tritium and Carbon 14) are lost, so as to define this β activity as non-volatile β activity; The total β activity was measured by liquid scintillation with a Packard mod. TriCarb 1000 instrument; The γ activity was measured by a solid scintillation detector (NaI).

Table 2 shows the main chemical and physical properties of the solvent waste components [16,17,19–21], where solvesso 100 (mixture of alkyl-benzenes) can be assimilated to mesitylene, owing to the very similar chemico–physical properties, and kerosene is considered as n-dodecane.

Laboratory scale tests were carried out both with simulated and genuine liquid waste.

The purpose of cold tests with simulated waste is the attainment of a fundamental understanding of distillation phenomena and the determination of all separation parameters to be used for the design of the real column.

The purpose of the so-called hot tests, with genuine waste, is essentially the assessment of the validity of simulated tests as well as the determination of the decontamination factors obtainable by separation.

Table 2
Main physical properties of solvent waste component

	M.W.[a]	Density[b] (kg m^{-3})	T_b^c (°C)	Flash point (°C)	C_p^d (cal g^{-1} °C^{-1})	Flammable limits in air (% vol)
Mesitylene	120.2	0.864	164.7	48	0.393	1–6
n-Dodecane	170.33	0.749	216	38	0.498	0.7–5
TBP	266.32	0.9724	289	145	0.41	–
TCA	392	0.81	365	168	–	–

[a]M.W. = molecular weight; [b]density at 25°C; [c]T_b = boiling point; [d]C_p = specific heat.

3.2. Experimental apparatus and procedures for cold tests

In order to obtain a full understanding of both the performance of distillation equipment and the fundamentals of distillation phenomena, the use of simulation distillation tests (e.g., air/water testing) can be an important tool for the assessment of distillation equipment [22].

As already pointed out, a series of simulation tests, here defined as 'cold tests', were carried out with simulated waste in order to accurately identify the hydraulic and physical parameters of the distillation (influence of packed height, reflux ratio, H.E.T.P., functionality, etc.) needed for the design of the real distillation column.

The whole equipment is made of borosilicate glass and consists of a reboiler having a total volume of 2×10^{-3} m^3, a distillation column, a condenser and a phase separator with sampling and reflux possibility for each phase.

The distillation column is a packed type column with Wilson spiral packing and with few ml hold up (Fig. 5). The main characteristics of the column are: internal diameter, 40 mm; packed height, 300 mm (max); Wilson spiral diameter, 6×7 mm.

Estimated height of packing equivalent to one theoretical plate (HETP), corresponds to 30–50 mm.

The apparatus was installed into a cold technological hall. Four series of tests were carried out with four different heights of packing:1st test series, $h = 0$ cm; 2nd test
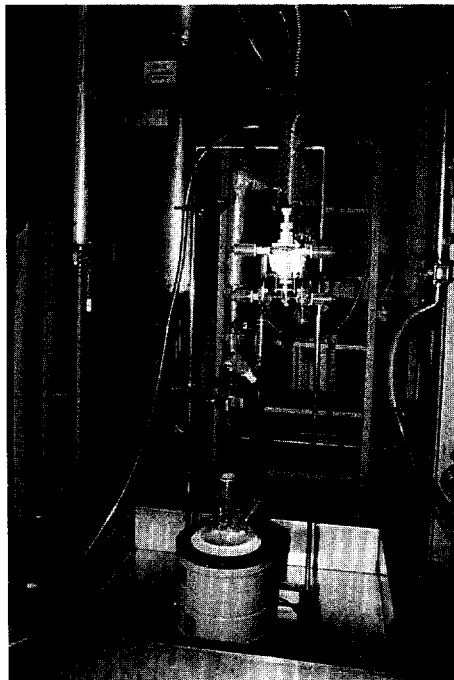

Fig. 5. Laboratory scale distillation apparatus.

series, $h = 5$ cm; 3rd test series, $h = 15$ cm; and 4th test series, $h = 30$ cm (max. height).

Only mesitylene was used instead of solvesso and mesitylene because of their very similar properties. Even if kerosene is a boiling fraction containing many tens of components, with potential increase in number with radiation damage, n-dodecane may be considered a simulant for kerosene good enough for the purpose of this work, as is reflected in the distillation behaviour obtained during cold and hot experimental runs.

About 1000 ml of simulated waste have been used for each test, with 500 ml of water added for the steam distillation.

The organic distillate was collected in fractions of 100 ml, each one analysed by HRGC. Qualitative and quantitative analyses were performed, the latter utilising the internal standard method. Two different reflux ratios were used for the organic distillate ($R = 0$ and $R = 1$), while the aqueous distillate was completely recirculated.

Preliminary wet oxidation tests were carried out by a borosilicate glass-stirred reactor having a volume of 5×10^{-2} m^3, equipped with on-line off-gas analyser, temperature, pH and level transducers. The off-gas analyses were realized by a Gas Chromatograph Dani mod. 8521 equipped with 2-m Poropack QS column, 2-m molecular sieve SM SA column and thermal conductivity detector HWD.

Gas chromatographic analyses of the organic phase were carried out by Perkin Elmer GC mod. 8700 equipped with capillary column and Flame Ionization Detector.

The composition of the simulated organic waste was as follows: TBP 55% v/v; TCA 42.5% v/v; kerosene 2.5% v/v.

3.3. Experimental apparatus and procedures for hot tests

The hot distillation tests were carried out inside a laboratory fume hood because of the low activity level of the waste. They were performed in order to evaluate the validity of the simulation and to verify the results forecast by means of the cold tests, as well as to highlight their strength and limitations.

The whole equipment employed was made of borosilicate glass following the same construction criteria adopted for cold tests.

In particular the distillation column is a packed-type column with Wilson spiral packing, few ml hold up and technical characteristics identical to the previous one. Estimated height of packing equivalent to one theoretical plate, corresponds to 30–50 mm.

The whole stage of hot distillation tests was divided into three series of experimental runs.

The first and second series of tests were carried out utilising batches of 855 and 640 ml of waste, with 200 and 300 ml of demineralized water added respectively.

The reflux ratio was set up at $R = 0$, while the total reflux was used for the aqueous phase. For each test the organic distillate were collected and analysed in fractions of 50–100 ml. Samples of water were also collected and analysed for Total α and Total β, always finding values below detection limits.

The duration of each distillation test, during these two series, was four or five working days.

In order to minimize the distillation time, a semicontinuous operation mode was set up for the third series of experimental tests, distilling about 5 l of genuine waste in each run. The experimental procedure was as follows: 1000 ml of organic waste were introduced into the reboiler together with 300 ml of demineralized water; the distillation was set up with the reflux ratio $R = 0$; total reflux has been used for the aqueous phase only; the organic distillate was collected in fractions of about 250 ml, corresponding to the quantity distilled during a working day. Each fraction was analysed in its chemical composition and activity content; for each fraction of 250 ml distilled at the end of the day, 250 ml of fresh organic waste was introduced to reintegrate the organic volume in the reboiler; when the fresh organic waste was finished the distillation was carried out until the distillate flow-rate was significant.

The duration of this stage of hot distillation tests was 19 working days. Therefore, 19 daily fractions were collected. The last fraction volume amounted to only 14 ml, a value which suggested operations to be stopped.

Samples of distilled water were also collected and analysed for Total α and Total β (volatile and non volatile).

4. Results and discussion

The distillation curves for each component and for each series of experimental runs performed during cold tests are reported in Figs. 6–9. Each experimental point is the average of five replicates.

In particular, Fig. 6 clearly shows that even without packing and organic reflux, the separation is quite good. Figs. 7–9 show that neither the organic reflux nor the height of packing appreciably affect separation because of the wide difference of boiling temperature of the components.
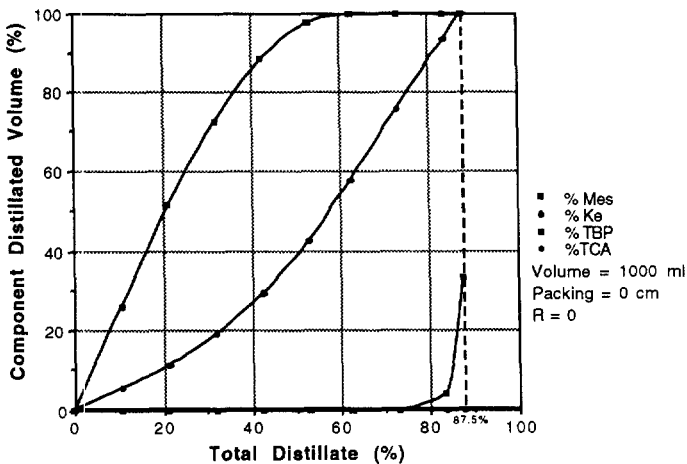

Fig. 6. Distillation curves during the first series of cold distillation tests.
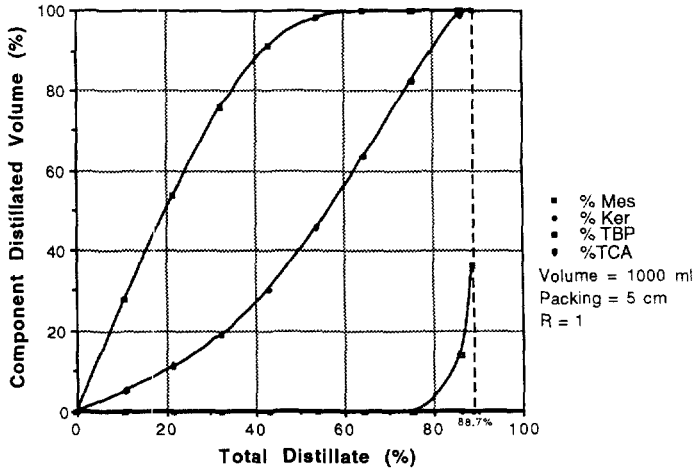
Fig. 7. Distillation curves during the second series of cold distillation tests.

On the basis of experimental data resulting from the first series of experimental runs (without packing material) the equilibrium curve of Fig. 10 was obtained, considering a binary system where light components (mesitylene + kerosene) are considered as a single key component A, and the heavy components (TBP + TCA) as a single key component B. In the same figure, we have superimposed the theoretical curve of Fig. 3. The two curves show a high degree of correlation, confirming the theoretical approach.

The main conclusion coming from the cold tests is that a flash distillation is quite sufficient for a good separation; the packing material can be used essentially as a high efficiency demister.
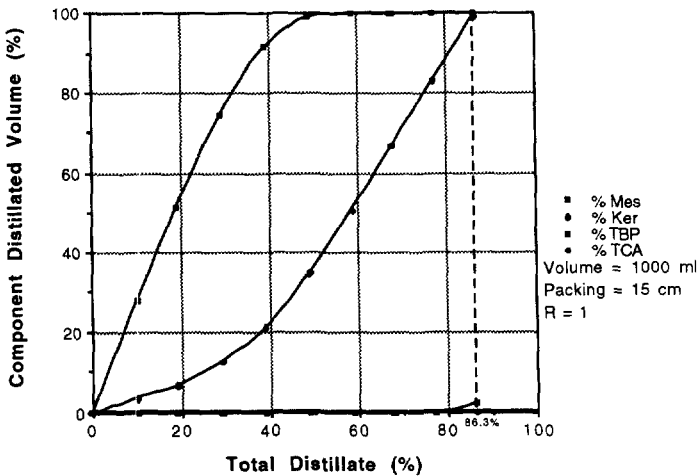

Fig. 8. Distillation curves during the third series of cold distillation tests.
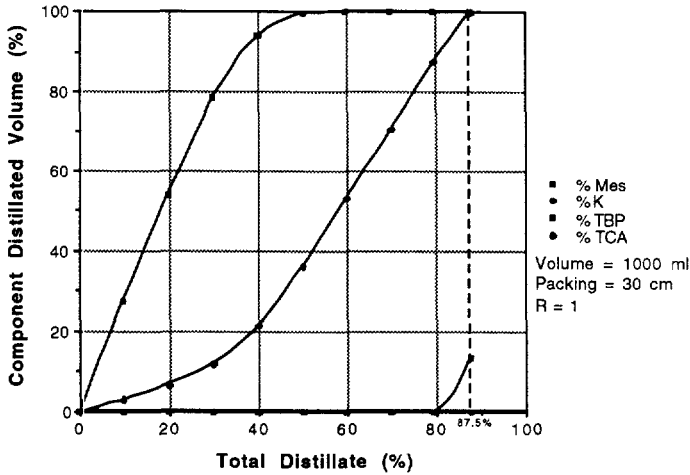
Fig. 9. Distillation curves during the fourth series of cold distillation tests.

With regard to the experimental runs performed with genuine solution, Tables 3 and 4 show the results of the first two series of hot tests, referring to volumes of distillate fractions and radiochemical data.

Samples of distilled water were also collected and analysed for Total α and Total β (volatile and non volatile), always finding values below the detection limits, as shown in Table 5, with reference to the third series of hot distillation tests.

Table 6 summarizes the main results of the hot distillation series of tests. It must be observed that very high decontamination factors have been achieved, especially for non volatile β and α, for which it must be also pointed out that the results of risen radioactivity have been calculated from the detection limits.
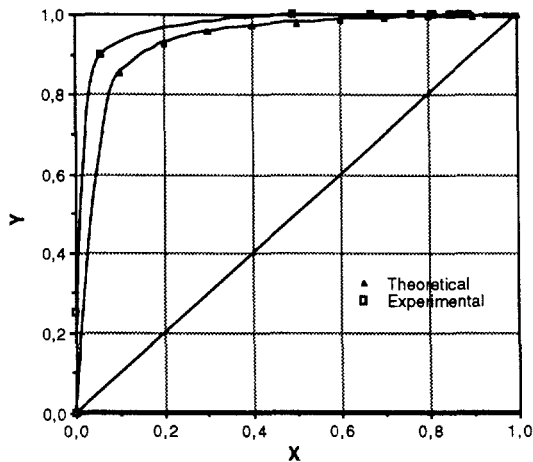

Fig. 10. Theoretical and experimental equilibrium curves with reference to the first series of cold experimental runs.

Table 3
Main data of 855 ml distillation (test series 1)

Fraction (No.)	Top T (°C)	Bottom T (°C)	Distillate			Activity		
			Fraction (ml)	Total (ml)	Total (%)	β (Bq l^{-1})	α (Bq l^{-1})	β n.v.[a] (Bq l^{-1})
1	96	100	50	50	5.8	800	2	< 15
2	96	100	100	150	17.5	350	< 1.5	< 15
3	96	100	50	200	23.4	700	4	< 15
4	96	100	90	290	33.9	400	< 1.5	< 15
5	97	100	55	345	40.3	200	2	< 15
6	98	100	100	445	52.1	250	< 1.5	< 15
7	98	100	50	495	57.9	280	5	< 15
8	98	100	90	585	68.4	300	< 1.5	< 15
9	98	100	50	635	74.3	850	< 1.5	< 15
10	98	100	90	725	84.8	850	< 1.5	< 15
11	98	100	15	740	86.6	3800	< 3	28.7
12	98	100	25	765	89.5	9650	11.6	104

[a] n.v. = non volatile.

With regard to the chemical composition of the streams resulting from distillation runs, we find out that residue contained mainly TPB (57.2% w/w) and TCA (42.7% w/w) and little kerosene (0.1% w/w), while distillate consisted of kerosene (61.2% w/w), mesitylene plus solvesso (36.2% w/w) and TBP (2.6% w/w).

Figs. 11–13 show the cumulative rising of activity during the distillation tests. At the end of the tests, when 88–90% of the waste has been distilled, less than 0.1% of the initial Total β is found in the distillate, about 0.01% for the β (n.v.) fraction and only

Table 4
Main data of 640 ml distillation (test series 2)

Fraction (No.)	Top T (°C)	Bottom T (°C)	Distillate			Activity		
			Fraction (ml)	Total (ml)	Total (%)	β (Bq l^{-1})	α (Bq l^{-1})	β n.v.[a] (Bq l^{-1})
1	95	100	50	50	7.8	< 200	6	< 15
2	96	100	100	150	23.4	< 200	< 1.5	< 15
3	97	100	50	200	31.2	< 200	2	< 15
4	97	100	100	300	46.9	< 200	< 1.5	< 15
5	97	100	50	350	54.7	< 200	< 1.5	< 15
6	97	100	100	450	70.3	< 200	< 1.5	< 15
7	97	100	50	500	78.1	< 200	< 1.5	< 15
8	97	100	55	555	86.7	2650	< 1.5	< 15
9	97	100	5	560	87.5	5450	3	< 15
Residue			80		12.5			

[a] n.v. = non volatile.

Table 5
Main data of 5 l distillation (test series 3)

Fraction (No.)	Top T (°C)	Bottom T (°C)	Distillate			Activity		
			Fraction (ml)	Total (ml)	Total (%)	β (Bq l^{-1})	α (Bq l^{-1})	β n.v.[a] (Bq l^{-1})
1	95	100	245	245	5.00	450	≤ 0.7	≤ 34
2	95	100	250	495	10.11	450	≤ 0.7	≤ 34
3	95	100	250	745	15.21	400	≤ 0.7	≤ 34
4	95	98	250	995	20.31	550	≤ 0.7	≤ 34
5	96	99	250	1245	25.42	550	≤ 0.7	≤ 34
6	97	99	250	1495	30.52	600	≤ 0.7	≤ 34
7	94	99	244	1739	35.50	650	≤ 0.7	≤ 34
8	98	99	250	1989	40.61	800	≤ 0.7	≤ 34
9	95	99	250	2239	45.71	900	≤ 0.7	≤ 34
10	95	102	250	2489	50.82	1000	≤ 0.7	≤ 34
11	95	102	248	2737	55.88	1000	≤ 0.7	≤ 34
12	97	102	250	2987	60.98	1100	≤ 0.7	≤ 34
13	96	102	250	3237	66.09	1500	≤ 0.7	≤ 34
14	96	102	250	3487	71.19	1350	≤ 0.7	≤ 34
15	96	102	250	3737	76.30	1400	≤ 0.7	≤ 34
16	96	102	250	3987	81.40	1400	≤ 0.7	≤ 34
17	96	102	250	4237	86.50	1250	≤ 0.7	≤ 34
18	96	102	82	4319	88.18	3000	2.5	≤ 34
19	96	102	14	4333	88.46	4100	5	≤ 34
Residue			565		11.54			

[a] n.v. = non volatile.

0.001–0.005% of the α activity. Each experimental point corresponds to the average of five replicates.

The data reported confirm the results obtained by other researchers in waste solvent distillation, i.e., by the French Nuclear Industry. The solvent distillation system operated in the UP3 plant allows the elimination of heavy degradation products of the solvent with the residue and the recycle of the solvent (TBP with a mixture of branched alkanes in which the main component is branched dodecane) with excellent extracting properties [23]. The process of solvent distillation in the new Cogema reprocessing plant of The Hague [24] results in significant improvements for throughput, end-products purification performances and waste minimisation. The distillation system developed for regeneration of Purex solvent [25], provides good separation of solvent degradation products. If compared with the above-mentioned results, this paper reports higher volume reduction of the liquid waste connected to high decontamination factors, thus allowing consistent savings for storage and disposal, as well as reduced risks related to possible unwanted events, for example. connected to the phase of transport [26].

In fact, as reported in Table 7, a remarkable aspect to be pointed out is the considerable reduction of the volume of radioactive wastes making the problem of storage and disposal far less expensive. At the same time an inherent safety approach to the problem is achieved by fulfilling the intensification criterion, that is, the reduction of

Table 6
Distillation hot tests main results

		Test 1	Test 2	Test 3
Waste				
Volume	(ml)	855	640	4898
Total β	$(Bq\,l^{-1})$	900,000	900,000	900,000
	(Bq)	769,500	576,000	4,408,200
β (n.v.)[a]	$(Bq\,l^{-1})$	176,000	176,000	176,000
	(Bq)	150,480	112,640	862,050
Total α	$(Bq\,l^{-1})$	52,500	52,500	52,500
	(Bq)	44,888	33,600	257,145
Distillate				
Volume	(ml)	765	560	4333
	(%)	89.5	87.5	88.5
Total β	$(Bq\,l^{-1})$	837	488	1000
	(Bq)	640	273	4333
	(%)	0.083	0.047	0.098
	D.F.	1202	2110	1017
β (n.v.)[a]	$(Bq\,l^{-1})$	≤ 18	≤ 15	≤ 34
	(Bq)	13.90	8.40	147.32
	(%)	0.009	0.007	0.017
	D.F.	10,826	13,410	5851
Total α	$(Bq\,l^{-1})$	≤ 3	≤ 3	≤ 0.7
	(Bq)	2.42	1.73	3.03
	(%)	0.005	0.005	0.001
	DF	18,587	19,422	84,780
Residue				
Volume	(ml)	90	80	565
	(%)	10.5	12.5	11.5

[a] n.v. = non volatile.

the amount of hazardous material in plant with a consequent increase in safety and reduction in cost [27].

The process results in smaller quantities of waste for ultimate disposal or treatment, with lower total treatment costs. If compared with different waste solvent treatment options [2], the proposed route is, especially with reference to the distillation step, a simple process with reduced requirement of interim storage. The possible problems remarked by Hutson, consisting in partial process and unsuitability of distillate for recycle, do not seem relevant in the application, as both residue and distillate are addressed to final disposal.

The remaining heavy fraction, characterised by a high contamination rate, can be treated by wet oxidation producing an aqueous solution containing all the activity to be conditioned and a non-radioactive gas stream to be discharged into the atmosphere, without any restriction, according to emission limits set down by EEC directives and national laws.

Wet oxidation processes are based on chemical demolition of organic substances by
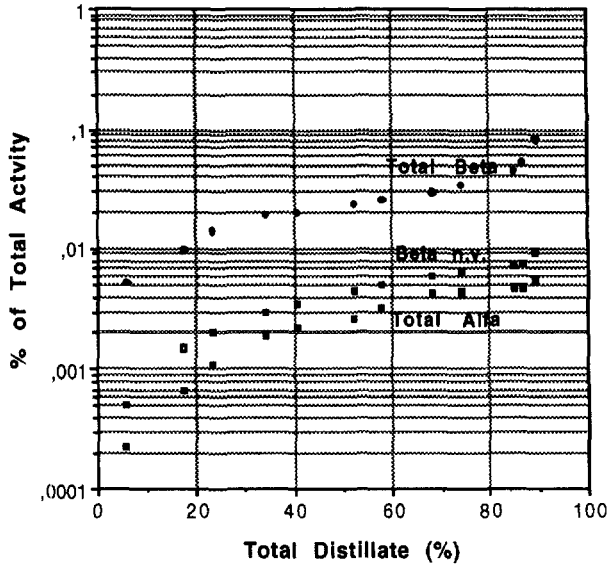
Fig. 11. Rising of activity with distillate, during the first series of hot distillation tests.

means of a strong oxidizing agent in aqueous media possibly in the presence of a catalyst, producing essentially water, carbon dioxide and inorganic salts. Wet oxidation techniques for application to radioactive waste streams have been investigated by a number of groups worldwide, sometimes with contrasting results [28].
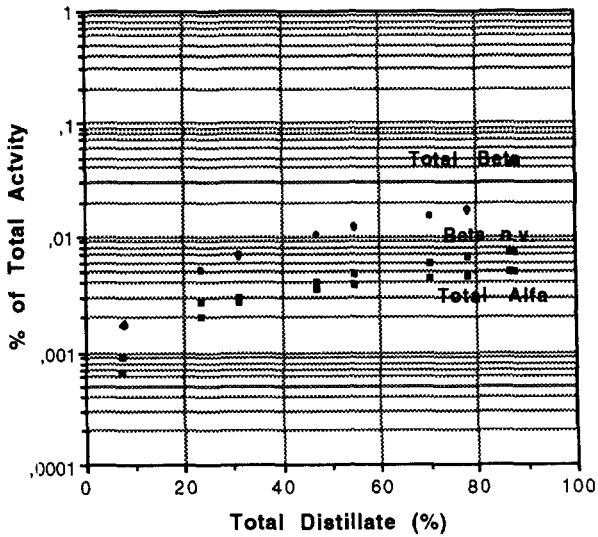

Fig. 12. Rising of activity with distillate, during the second series of hot distillation tests.
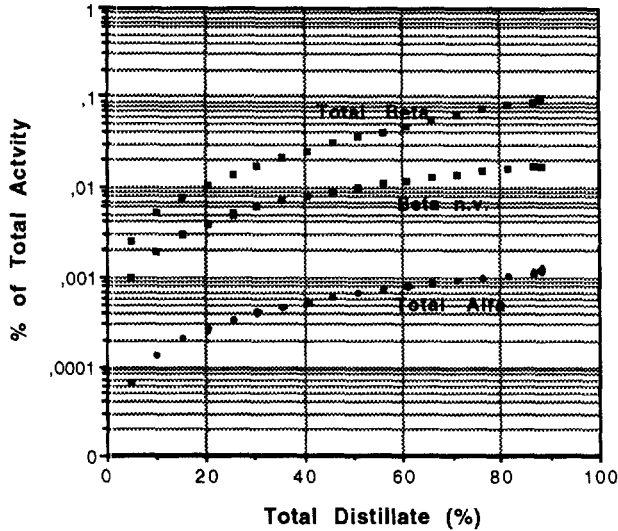
Fig. 13. Rising of activity with distillate, during the third series of hot distillation tests.

Especially suitable for radioactive organic waste is wet oxidation, by means of hydrogen peroxide in the presence of catalysts like ferrous salts:

$$\text{Organic substance} + H_2O_2 \xrightarrow{(Fe^{++})} CO_2 + H_2O + \text{Inorganic salts} \tag{5}$$
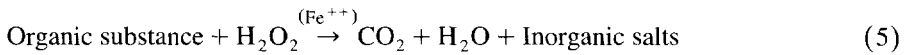
The iron/H_2O_2 oxidative mixture is universally known as Fenton's reagent [29] and widely experimented for radioactive organic waste treatment during the last decade.
The mechanism of oxidation seems to be as follows [30]:

$$H_2O_2 + Fe^{2+} = Fe^{3+} + OH^- + HO^{\cdot} \tag{6}$$

The hydroxyl radical is responsible for the oxidation of the organic matter with several radicalic reactions as hydrogen abstraction, oxygen addition and so on, resulting in a progressive breakdown of the organic molecules.

Table 7
Distribution of the activity

	Total β (Bq)	β (n.v.)[a] (Bq)	Total α (Bq)	Volume (l)
S.W.[b]	$2.25E+10$	$4.39E+09$	$1.31E+09$	25,000
Distillate	$2.21E+07$	$7.52E+05$	$1.55E+04$	22,125
	($df \geq 1000$)	($df \geq 5000$)	($df \geq 50,000$)	(88.5%)
Residue	$2.25E+10$	$4.39E+09$	$1.31E+09$	2875

[a] n.v., non volatile radionuclides; [b] S.W., solvent waste; df, decontamination factor.

Of course there are also series of parallel reactions which promote the unwanted decomposition of the hydrogen peroxide to oxygen and water. For example:

$$H_2O_2 + HO \cdot = H_2O + HOO \cdot \tag{7}$$

$$HOO \cdot + Fe^{3+} = Fe^{2+} + H^+ + O_2 \tag{8}$$

which reproduces the Fe(II) species so as to promote a chain reaction but it is also possible for the following reaction to occur:

$$HO \cdot + Fe^{2+} = OH^- + Fe^{3+} \tag{9}$$

which stops the chain reaction.

This brief description shows that the reaction mechanisms are very complex and not completely known.

A wet oxidation process for treatment of TBP/kerosene waste was developed by NAIG, Japan [31], using different catalysts (mainly iron and copper salts).

Although the authors claimed destruction of both TBP and kerosene, reproducibility of the results seems to be not proven by ENEA preliminary trials, which demonstrated an apparent unreactivity of kerosene [32,33]. The results of preliminary wet oxidation experimental runs carried out on a simulated waste volume of 2×10^{-3} m^3, are reported in Fig. 14, with reference to the reaction behaviour of each component. Average consumption of hydrogen peroxide in the presence of 40 g $FeSO_4$ and 0.83×10^{-3} m^3 H_2SO_4 (96% v/v) corresponded to 32×10^3 kg H_2O_2/m^3 waste. H_2O_2 utilization efficiency, expressed as $(\%CO_2/\%CO_2 + \%O_2)$ is reported in Fig. 15, corresponding to a total experimental time of 9 h. The main conclusions of preliminary tests are as follows:

- The exothermicity of the reaction allows the reactor to be kept at the optimal operating temperature of 98–100°C;
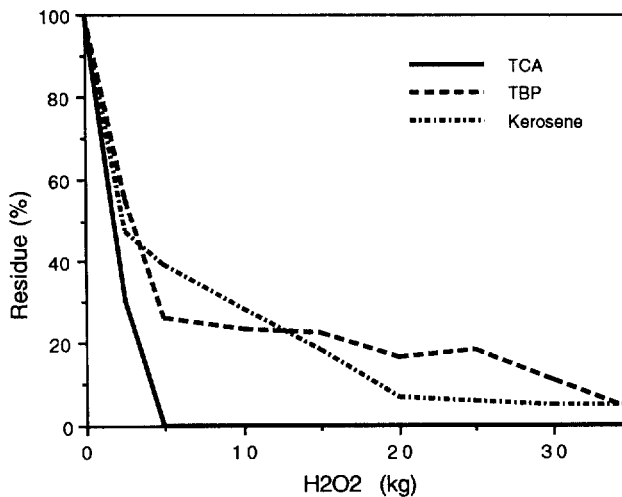

Fig. 14. Wet oxidation behaviour of each component of simulated waste having a total volume of 2×10^{-3} m^3.
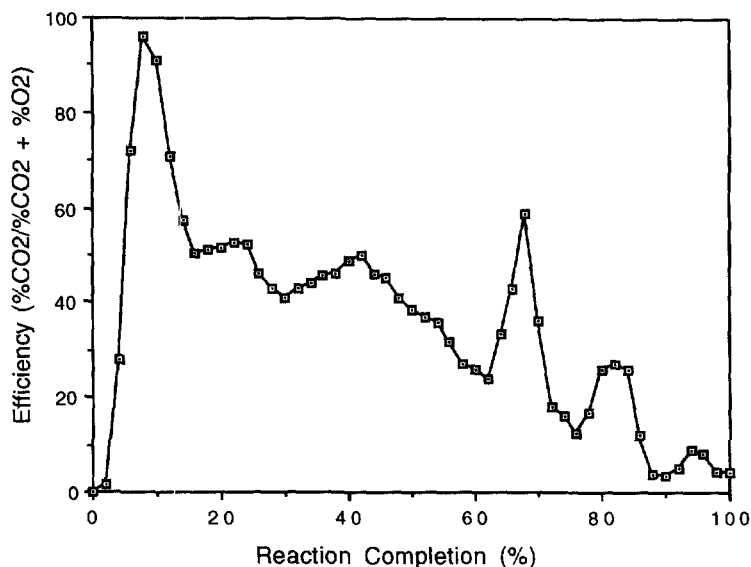
Fig. 15. Hydrogen peroxide utilization efficiency, corresponding to total experimental time of 9 h, with simulated waste having a volume 2×10^{-3} m^3.

- TCA appears to be the most reactive component of the mixture as it decomposes in nearly 5 h in intermediate molecules;
- The low reactivity to wet oxidation, of kerosene with hydrogen peroxide, part of which was found in the vapor phase, confirmed the essential role of the previous distillation step.

These preliminary results agree with AEA Technology (UK) [6].

At the moment AEA Technology has focused its research on the application of wet oxidation to the treatment of spent ion-exchange resins, and is now at the stage of mobile pilot plant [34]. On the contrary the efforts of the present research line are focused on the radioactive spent solvent treatment, after separation performed by distillation.

We can resume the main features of the wet oxidation process in the following main points: the process is simple, easy and inherently safe, in accordance with the attenuation criterion [27], being carried out at atmospheric pressure and low temperature (up to about 100°C, boiling point of the aqueous phase); transformation of the organic waste into gaseous products and aqueous solutions (CO_2, H_2O, inorganic salts); the aqueous residue, containing all the radioactivity, can be cemented producing a form suitable for long-term storage.

5. Conclusions

Techniques developed in this study provide a useful management tool for radioactive liquid wastes. The present research work confirms the feasibility of the distillation

process in order to obtain a substantial volume reduction of the initial waste. Moreover, the validity of simulation runs enhance the possibility of conducting full-scale tests with simulated solution in order to investigate the most important phenomena affecting the performance of an industrial packed column without the risks connected to the handling of radioactive solutions.

The reported experimental results in terms of the entire stock of solvent waste to be distilled, including the global partition of the activity between the streams, prove the feasibility of the process for reduction of hazardous waste to be treated by wet oxidation or by other options, according to an inherent safety approach, by means of the intensification criterion.

More than 88% of the solvent waste can be distilled with a negligible rising of activity, so the top product of the distillation can be conventionally incinerated and its combustion gases discharged into the atmosphere without any filtration, according to the emission limits for the plant, set down by EEC as well as national laws.

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