



Oxidative Degradation of Low and Intermediate Level Radioactive Organic Wastes 2: Effect of Acid Carbonization on The Decomposition of Spent Ion - Exchange Resins

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خلاصة

تقدم الدراسة الحالية طريقة اقتصادية وبسيطة وذات فعالية عالية للتكسير الكيميائي للمخلفات العضوية الصلبة وبخاصة المبادلات الايونية المستهلكة وتهدف هذه الدراسة إلى التوصل إلى اختزال حتمي مناسب وكذلك تجنب المشكلات التقنية التي تلازم الطرق المشابهة (كالحرق في وجود كميات مختلفة من الأوكسجين).

وقد تمت دراسة العوامل التي تؤثر في الأكسدة التحليلية للمبادلات الايونية في وسط حمضي باستخدام فوق اكسيد الهيدروجين كمادة مؤكسدة وبالاخص تأثير وقت المعالجة وكذلك نسبة المبادلات الأيونية الى حامض الكبريتيك وذلك على المستوى المعمل كما تم تحليل الغازات المتصاعدة أثناء عملية التكسير.

Abstract

The present work provides a simplified, effective and economic method for the chemical decomposition of radioactively contaminated solid organic waste, especially spent ion - exchange resins. The goal is to achieve volume reduction and to avoid technical problems encountered in processes used for similar purposes (incineration, pyrolysis).

Factors affecting the efficiency and kinetics of the oxidation of the ion exchange resins in acid medium using hydrogen peroxide as oxidant, namely, time of treatment and the acid to resin ratio were studied systematically on laboratory scale level. Moreover the percent composition of the off - gas evolved during the decomposition process was analyzed.

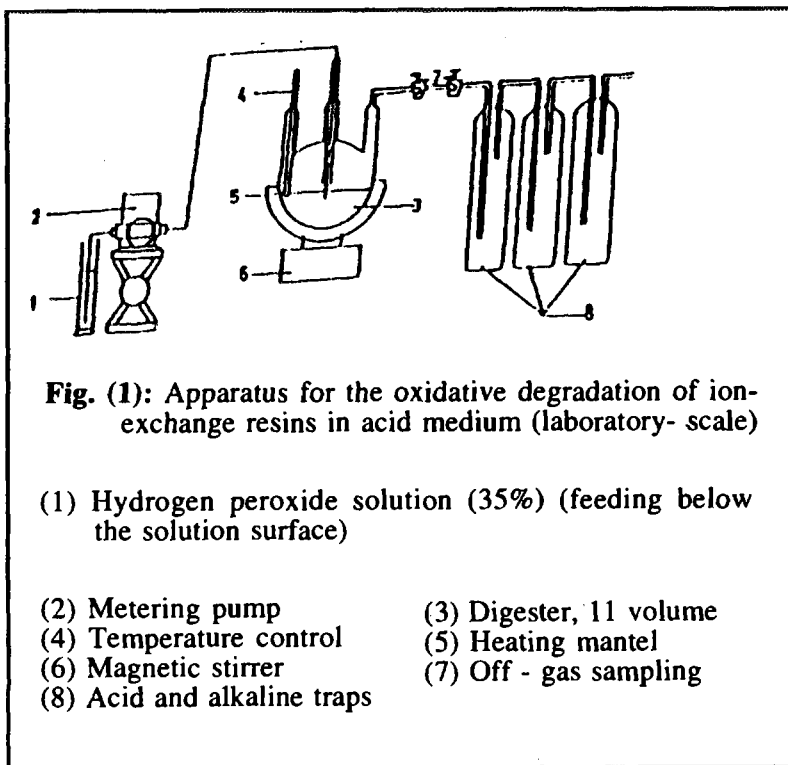
1. Introduction:

Acid digestion is a potentially attractive technique for volume reduction of solid hazardous wastes and although its essential application area is the alpha - bearing waste, yet, the method can be in principle used to reduce the volume of ion exchange - resins as well [1]. The digestion process is a method that traditionally involves the dehydration of ion - exchange resins and to oxidize the carbon by means of nitric acid [2-4], or hydrogen peroxide [5, 6]. Although this process has been investigated on laboratory - and bench - scale test units, yet, it has reached the stage of industrial application in many nuclear power plants in different countries [7-10]. In case of using nitric acid as oxidant, the evolution of nitrogen and nitrogen oxide gases complicate the off - gas treatment and need an additional system for nitric acid recovery.

In the work reported hydrogen peroxide was used instead of nitric acid for oxidative degradation of spent ion - exchange resins to avoid these problems [7,11]. The main goal of this study was to evaluate the role of the concentrated sulphuric acid during the charring and oxidation of the ion - exchange resins

2. Experimental Approach :

A calculated weight of S100 KR/H cation and M500 KR/OH anion Lewatit ion exchange resin, mixture (1 : 1 by weight), supplied by Bayer, and a given volume of technical grade (98%) concentrated sulphuric acid were charged into one liter three neck digestion flask. The flask was heated, using a heating mantel, up to 240°C. When the presumed temperature was reached hydrogen peroxide (35%) was added beneath the solution surface using metric pump. The system was equipped with acidic and alkaline traps to hold back the evolved gases during the reaction stream Fig (1). Samples from the off-gas stream were collected before the trap every 30 minutes and analyzed using AREOGRAPH Series 3700- TCD - FID gas Chromatography.



The elemental analysis and the water content of the cation and anion resins were represented in table I. Additional information concerning the characteristics of the resin were mentioned in pervious publication [12].

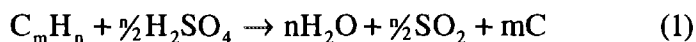
Table I: Water Content And Elemental Analysis of Ion Exchange Resins.

Resin type	Assumed basic unit	Water content% by weight	C%	H%	N%
Cation resin	C_8H_7	45.25	5.18	5.2	0.8
	SO_3H	56.63	74.6	8.6	4.1

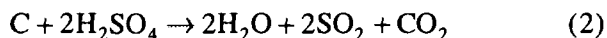
3. Result & Discussion

The work reported is part of a comprehensive research and development program to study the treatment [12] and immobilization [13-15] processes of ion - exchange resins (IXR). Different factors affecting both processes have been studied and the data were previously published [12-15]. In the present study oxidative degradation of ion - exchange resins (IXR) in sulphuric acid - hydrogen peroxide mixture was carried out at relatively lower temperature (240°C) compared with dry oxidation process (incineration & pyrolysis) [16]. Heating is needed to start the oxidation reaction where the net heat input must exceed the difference between the heat absorbed in the endothermic reactions e.g. vaporization of the reactant and the heat evolved in the exothermic reactions e.g. decomposition, oxidation.. [17]

Heating the organic IXR (C_mH_n) in H_2SO_4 results in its charring (mC). The chemical reactions expected to take place according to those given in the literature [11, 18, 19] were as follows:



Continuous heating of the previous mixture results in subsequent partial oxidation of the formed carbon to CO_2 :



Increasing the heating time in conc. H_2SO_4 ., increases the oxidation of the formed carbon which is reflected in the percentage of carbon oxides in the off- gas, Table II. It is clear, also, from the data obtained in table II that the average percentage of carbon monoxide (CO) in the off- gas during the preheating time was in most cases insignificant compared with that of carbon dioxide (CO_2)

The addition of H_2O_2 to the system leads to more oxidation of the formed carbon (mC) to CO and CO_2 according to the following equations:

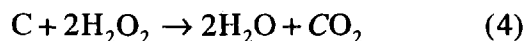
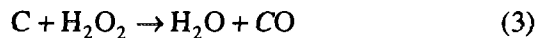



Table II: oxidative Degradation of Ion - Exchange Resins In Acid Medium.

The effect of pretreatment processes on the variation of off- gas composition as a function of reaction time.

reaction time (min)	A			B			C		
	O ₂ %	CO %	CO ₂ %	O ₂ %	CO %	CO ₂ %	O ₂ %	CO %	CO ₂ %
30	9.3	8.4	37.7	2.2	2.0	52	0.5	1.8	23.9
60	10.5	14.1	53.3	3.3	5.0	66.3	3.1	11.0	69.6
90	24.8	12.6	56.1	23.8	12.6	53.7	3.2	13.1	79.2
120	24.1	13.2	52.8	62.8	8.9	16.8	14.8	16.3	6.75
150	75.5	6.2	8.6	27.4	2.6	7.3	39.5	1.3	3.6
180	91.5	2.8	0.2	—	—	—	—	—	—
210	—	3.8	0.4	—	—	—	—	—	—
240	—	—	—	—	—	—	—	—	—
270	—	—	—	—	—	—	—	—	—
300	—	—	—	—	—	—	—	—	—

reaction time (min)	D			E			F		
	O ₂ %	CO %	CO ₂ %	O ₂ %	CO %	CO ₂ %	O ₂ %	CO %	CO ₂ %
30	—	0.3	16.7	0.1	0.3	21.5	0.1	0.8	20.9
60	0.1	0.4	19.2	0.1	0.8	26.7	0.1	0.4	24.0
90	2.1	8.8	63.1	0.1	0.6	28.3	0.1	—	27.8
120	7.5	9.1	51.9	2.9	8.2	63.0	1.5	2.5	34.3
150	3.4	11.8	71.9	3.1	10.2	66.6	2.3	6.5	57.3
180	9.8	12.3	66.7	3.5	12.0	70.8	3.3	12.4	56.7
210	30.3	1.2	4.0	8.5	13.5	70.5	3.5	12.2	65.3
240	—	—	—	36.5	13.3	47.4	11.8	14.7	66.4
270	—	—	—	28.1	1.2	4.0	57.3	10.5	21.5
300	—	—	—	—	—	—	52.3	1.2	2.4

 before H₂O₂ addition

- (1) 20g bead resins (1:1 cation to anion by weight) contain 12.64g carbon.
- (2) Reaction temperature: 240°C.
- (3) Rate of H₂O₂ addition: ≈ 1.2 ml /min.
 - A) Start heating and H₂O₂ addition at the same time.
 - B) H₂O₂ addition at 240°C directly.
 - C) heating for 30 min. before H₂O₂ addition.
 - D) heating for 60 min. before H₂O₂ addition.
 - E) heating for 90 min. before H₂O₂ addition.
 - F) heating for 120 min. before H₂O₂ addition.

The chemical equations (1 -4) and the data represented in table II indicate that CO₂ in the off - gas was formed through two oxidation processes namely oxidation of carbon with hot H₂SO₄ and with H₂O₂ added while CO was mainly formed through the oxidation with H₂O₂. This explain the higher percentage of CO₂ in the off - gas compared with CO %, Table II. With continuous addition of H₂O₂ to the system the oxidation products, (CO % & CO₂ %), increased with increasing the oxygen (O₂) supply to reach its maximum and then decreased due to the consumption of the carbon contained in IXR loaded, Fig (2). A remarkable increase in the O₂ % in the off-gas at the end of the reaction indicates that the oxidation process was approaching its end, Table (2). This was also accompanied by the decrease in the main oxidation products (CO % & CO₂ %), Fig (2). The total percentage of the main oxidation products, (CO% + CO₂%), for samples where H₂O₂ added directly at 240°C (i.e without preheating period) reached its maximum after 60 minutes Fig (2). The delay in reaching the maximum percentage of the total oxidation products for the preheated samples compared with that untreated one may be attributed to the preheating time, Fig (2).

The data obtained in case of simultaneous heating and addition of H₂O₂ to the system are given in table III, where the time required to complete the oxidation of a given weight of IXR was 220 minutes and the volume of H₂O₂ consumed was 260 ml. Comparing these results with those in case of addition of H₂O₂ after the temperature of the system reached 240°C it is clear that: the oxidation time was reduced to 150 minutes and the consumed H₂O₂ to 180 ml. Preheating IXR in hot acid for different periods before introducing H₂O₂ results in an additional reduction in the oxidation time by 20% and H₂O₂ consumption by

22.2%. (From 150 minutes to 120 minutes and H₂O₂ from 180 ml to 140 ml), Table III.

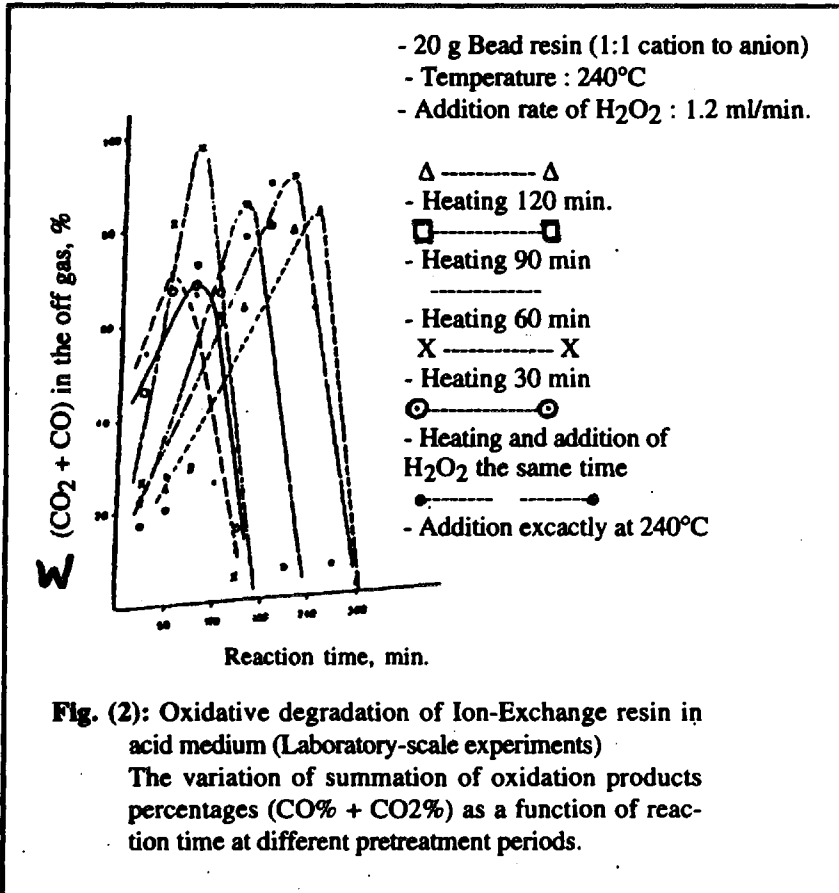


Table III: Oxidative Degradation of Ion - Exchange Resins In Acid Medium

The effect of pretreatment conditions on the oxidation process.

Pretreatment Conditions	Oxidation Time (min)	H ₂ O ₂ consump. (ml)
Start heating and addition	220	260
addition of H ₂ O ₂ at 240°C	150	180
addition of H ₂ O ₂ after heating at 240°C for 30 min.	150	180
addition of H ₂ O ₂ after heating at 240°C for 60 min.	140	170
addition of H ₂ O ₂ after heating at 240°C for 90 min.	135	150
addition of H ₂ O ₂ after heating at 240°C for 120 min.	120	140

(1) 20g bead resin (1:1 cation to anion by weight) contain 12.64g carbon.

(2) Reaction temperature : 240°C

(3) Rate of H₂O₂ addition: ≈ 1.2 ml /min.

Although the weight of oxidized carbon in gram per minute (oxidation rate), was increased by increasing the preheating time before H₂O₂ addition, yet, the sulphate content in the off - gas was also increased more than 5 fold Table IV. The sulphate aerosols produced during the oxidation course could be carried mechanically and complicated the off- gas treatment rather than their corrosive and pollution effects.

Therefore, it was concluded that addition of oxidant directly after raising the temperature of ion-exchange resins/sulphuric mixture to 240°C seems to be more suitable

Table IV: Oxidative Degradation of Ion - Exchange Resins In Acid Medium

The effect of pretreatment conditions on the sulphate content:

Pretreatment Conditions	Oxidation Rate g (carbon/min)	Sulphate Content in off-gas (g/l)
Start heating and addition	0.070	0.13
addition of H ₂ O ₂ at 240°C	0.105	5.22
addition of H ₂ O ₂ after heating at 240°C for 30 min.	0.105	24.46
addition of H ₂ O ₂ after heating at 240°C for 60 min.	0.113	25.60
addition of H ₂ O ₂ after heating at 240°C for 90 min.	0.117	27.20
addition of H ₂ O ₂ after heating at 240°C for 120 min.	0.132	28.80

- (1) 20g bead resin (1:1 cation to anion by weight) contain 12.54g carbon
- (2) Reaction temperature : 240°C
- (3) Rate of H₂O₂ addition: ≈ 1.2 ml /min.

Increasing the amount of IXR added to a given volume of H₂SO₄ increased the total oxidant consumption and the time required to complete oxidation, Table V. In fact the result obtained was expected, since, increasing the amount of IXR feeded to the system increased the carbon content per unit volume of the reaction mixture and will in turn, increase the total volume consumed of H₂O₂ and the time required for oxidation. The variation in the volume of H₂O₂ in ml/g resin and consequently per gram carbon was not significantly high for an increase of 150% in the amount of carbon added to the system. This indicates that the volume of oxidant consumed per gram resin or carbon, (in the range of the ratios used), was independent on the IXR/H₂SO₄ ratio. In the same time, the oxidation rate in gram resin per minute and in gram

carbon per minute were not highly affected with increasing the amount of IXR introduced to the system Table V.

The total carbon remaining in both solid and liquid phases at the end of the reaction increased with increasing the amount of IXR decomposed Fig (3). Increasing the amount of IXR feeded to the system from 40 to 60 g/l decreased the total conversion from 99.42% to 99.12%. on the other hand increasing the feeded IXR to 100 g/l decreased the total conversion to 97.48%. This indicates that a concentration of IXR lower than 60 leads to a conversion higher than 99 %. Based on the obtained data in table V, it was recommended not to exceed: 16.6 (60 g/l) resin / acid ratio.

The amount of unoxidized carbon detected in the liquid phase at the end of the reaction was always relatively higher than those detected in the solid residue independent on the IXR / acid ratio Table V

The data so far obtained show that the formed inorganic residue contains relatively low concentration of organic matter which is favorable for the subsequent handling and immobilization process of the residue after the proper pretreatment process (neutralization).

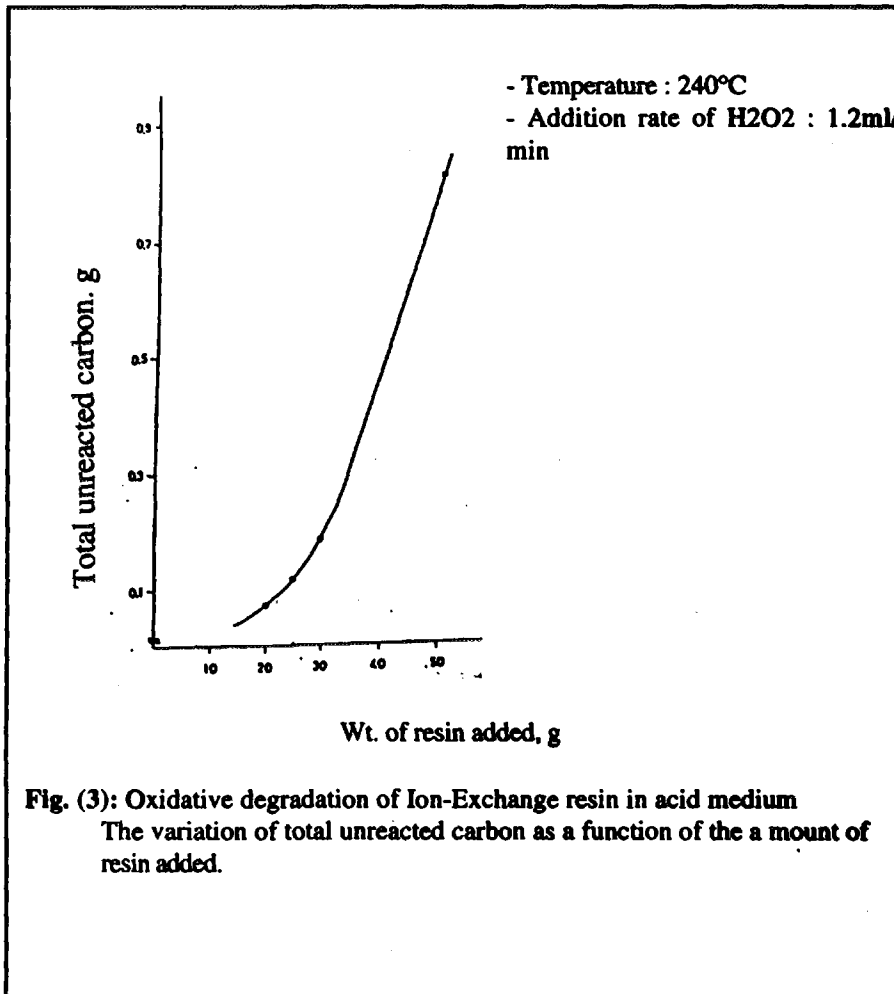


Fig. (3): Oxidative degradation of Ion-Exchange resin in acid medium
The variation of total unreacted carbon as a function of the amount of resin added.

Table V: Oxidative Degradation of Ion - Exchange Resin In Acid Medium
The effect of resin : acid ratio on the oxidation process

Resin added			oxidation time (min)	H ₂ O ₂ consumption		oxidation rate		Solid Residue			Unreacted Carbon					
g	resin H ₂ SO ₄	g carbon		ml/g resin	ml/g carbon	g/resin/ min	g/carbon/ min	weight g	weight reduction %	factor	In solid wtg conversion %		In liquid wtg conversion %		Total wtg conversion %	
20	1:25	12.64	108	6.5	10.29	0.19	0.12	0.0154	99.9	1000	0.0073	99.94	0.066	99.48	0.0733	99.42
25	1:20	15.80	150	7.2	11.39	0.17	0.11	0.157	99.9	1000	0.0074	99.95	0.1095	99.31	0.1169	99.26
30	1:16.6	18.96	175	7.0	11.08	0.17	0.11	0.0677	99.8	500	0.0290	99.85	0.1375	99.28	0.1665	99.12
50	1:10	31.60	300	7.2	11.39	0.17	0.11	0.1016	99.8	500	0.0440	99.86	0.753	97.62	0.797	97.48

- (1) 500 ml of concentrated sulphuric acid.
- (2) Reaction temperature : 240°C
- (3) Rate of H₂O₂ addition : ≈ 1.2 ml/min.

Although the weight of residue increased with increasing the amount of resin digested in a given volume of H_2SO_4 yet the weight reduction percentages were higher than 99.8 and the reduction factors were always higher than 500 for all the ratios used, Table V. These values for weight reduction were in favor of the oxidation process of IXR using H_2O_2 compared with those using nitric acid [20] or dry oxidation e.g. incineration [21] and pyrolysis [16]

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