

Oxidation Kinetics of Spent Low-Level Radioactive Resins

Y.-J. Huang*

*Chung Hwa College of Medical Technology
Department of Safety Health and Environmental Engineering
Tainan County, Taiwan 71741*

H. Paul Wang

*National Cheng Kung University, Department of Environmental Engineering
Tainan, Taiwan 70101*

Chih C. Chao

*Industrial Technology Research Institute, Center for Environmental
Safety and Health Technology Development, Hsinchu, Taiwan 310*

H. H. Liu

*Chung Shan Medical University, Department of Occupational Safety and Health
Taichung, Taiwan 402*

M. C. Hsiao

*Kun Shan University of Technology, Department of Environmental Engineering
Tainan, Taiwan 710*

and

S. H. Liu

*National Cheng Kung University, Department of Environmental Engineering
Tainan, Taiwan 70101*

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Abstract—Experimentally, two-stage oxidation of spent low-level radioactive resin was found by thermogravimetric analysis (TGA). About 24% of the spent resins was oxidized at 600 to 900 K. Online Fourier transform infrared spectra showed that the decomposition of the $-SO_3H$ species in the resin to SO_2 occurred at 670 and 1020 K. The numerical calculation from TGA weight loss data at different heating rates showed that the global activation energies for oxidation of the spent resins were 108 to 138 $\text{kJ}\cdot\text{mol}^{-1}$. The reaction orders for resin and oxygen were about 1.0 and 3.5, respectively. The global rate equations for oxidation of the resin in the first and second stages can be expressed as dx_1/dt (s^{-1}) = 2.3×10^7 (s^{-1}) $\exp[-117900(\text{J}\cdot\text{mol}^{-1})/T(\text{K})][1-x(\%)]^{0.82} [O_2(\text{vt}\%)]^{3.5}$ (x denotes the reaction conversion) and $dx_2/dt = 8.4 \times 10^{17} \exp(-239500/RT) (1-x)^{0.9} [O_2]^{4.5}$, respectively.

I. INTRODUCTION

Ion exchange resins are widely used in filter-demineralization units to remove radioactive pollutants

in nuclear power plants.¹ Instead of regeneration, the spent resins are generally stored in high-integrity containers. Treatments of the resin wastes by conventional cement-solidification methods have not been very effective. Currently, it is inevitable that storage sites need to be expanded or the volume of low-level radioactive (LLRA) wastes needs to be reduced.

*E-mail: yuh205@lehigh.edu

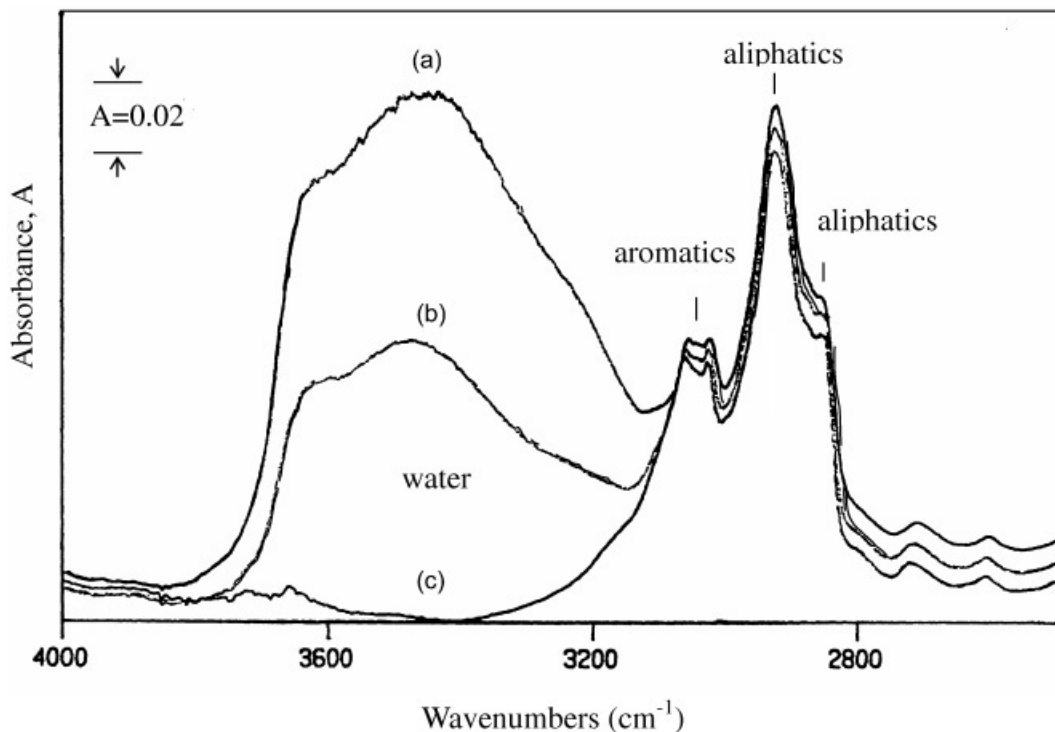


Fig. 1. In situ DRIFT spectra for oxidation of the resin at (a) 303, (b) 473, and (c) 723 K.

Incineration, supercritical water oxidation, pyrolysis, and catalytic incineration have been used to reduce the volume of the LLRA spent resin.²⁻⁸ However, literature still lacks basic oxidation kinetic data for decomposition of the LLRA spent resin. The main reaction kinetic parameters [such as activation energy (E_a), pre-exponential factor, and reaction order] can be derived from simple thermogravimetric analysis (TGA) data that can be treated by the classical laws of kinetics.⁹⁻¹⁶ Detailed descriptions of these methods have been given by Friedman.¹¹ Petrovic and Zavargo¹² also evaluated the kinetic parameters from the TGA traces. Generally, kinetic studies have been conducted in inert or vacuum atmosphere.^{10,14} Oxidation kinetics has received relatively less attention.¹⁴ Thus, the main objective of this work was to investigate oxidation kinetics of the spent LLRA resins by the TGA method. Structural changes of the resin during oxidation were also studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

II. EXPERIMENTS

The cation-exchange resin (Powdex)^a was provided by the Taiwan nuclear power company. The spent resin

generally contains moisture (42%), sulfur (5%), ash (16%), and base copolymers of styrene and divinyl benzene (37%). The resin samples having particle sizes of 30 to 80 and 250 to 300 meshes (coarse and fine resin, respectively) were used in the TGA experiments, which were conducted on a thermogravimetric analyzer.^b Prior to the TGA experiments, the resin samples were dried at 343 K for 16 h to have a water content of $\sim 12\%$. About 10 mg of the dried resin was oxidized at a heating rate of 4, 5, or 8 $\text{K} \cdot \text{min}^{-1}$ in the 100 ml/min high-purity air (4.2 to 21% O_2) at 300 to 1173 K in the TGA experiments. The weight of the resin was recorded at a 10-s interval. The calibration procedures for the TGA/differential thermal analysis baseline and temperature were performed once a month. In all experiments, aluminum oxide was used as a temperature reference.

Product gases from the temperature programmed oxidation of the resin were analyzed by online Fourier transform infrared (FTIR) spectroscopy. Infrared spectra were recorded on an FTIR spectrometer (FTS-40) with fully computerized data storage and data-handling capability. For all spectra reported, 64-scan data accumulation was carried out at a resolution of 4 cm^{-1} . Structural changes of the resin during oxidation at elevated temperatures (303 to 723 K) were also studied by in situ DRIFTS.

^aThe cation-exchange resin is manufactured by the DOW Chemical Company.

^bThe thermogravimetric analyzer is the SDT 2960 model, manufactured by TA Instruments.

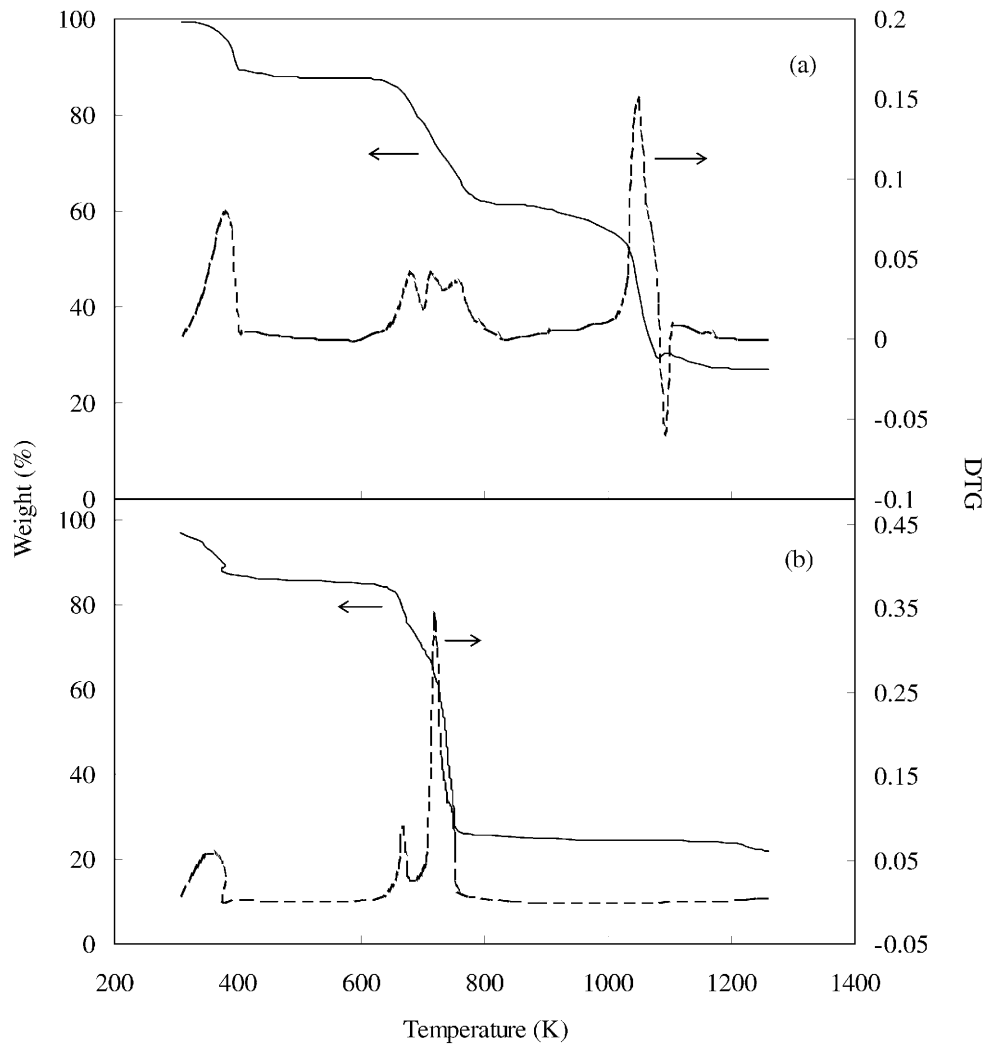


Fig. 2. TGA for oxidation of (a) coarse (30 to 80 mesh) and (b) fine (250 to 300 mesh) resins.

III. RESULTS AND DISCUSSION

The DRIFT spectra for oxidation of the resin at 373 to 673 K are shown in Fig. 1. The absorbance of moisture at 3600 to 2900 cm^{-1} decreased significantly during the oxidation process. A small amount of aromatics (3020 to 3080 cm^{-1}) and aliphatics (2840 to 2920 cm^{-1}) of the resin was oxidized. The FTIR spectra also show that olefins (2830 cm^{-1}) and paraffins (2870 cm^{-1}) in the resin were also involved in oxidation at 673 K.

Typical TGA curves for oxidation of the resin at 300 to 1173 K are shown in Fig. 2a. Dehydration of the resin with a weight loss of 12% occurred at ~ 360 K. Two-stage oxidation of the resin at 600 to 1173 K was found in the oxidation process. In the first stage, $\sim 29\%$ of the resin was oxidized at 600 to 900 K. At 900 to 1173 K, in the second stage, a weight loss of 31% was observed.

The oxidation residue was $\sim 28\%$ at >1173 K. Figure 3a shows the temperature dependence for the yield of SO_2 (monitored by online FTIR spectroscopy) in the resin oxidation process. In the first stage, sulfonic acid groups ($-\text{SO}_3\text{H}$) of the resin were decomposed into gaseous SO_2 that led to a weight loss of 13%. The oxidation of hydrocarbons corresponded to a weight loss of $\sim 16\%$. In the second stage, the weight losses for decomposition of SO_4 and oxidation of hydrocarbons were 8 and 23%, respectively.

In a parallel experiment, in order to reduce the possible mass transfer limitations, oxidation of the fine resin (250 to 300 mesh) was also studied. In Fig. 2b, oxidation of the fine resin was highly enhanced. Table I summarizes the weight losses for oxidation of coarse and fine resins. The oxidation enhancement for the fine resin might be due to the accelerated decomposition of $-\text{SO}_3\text{H}$ species

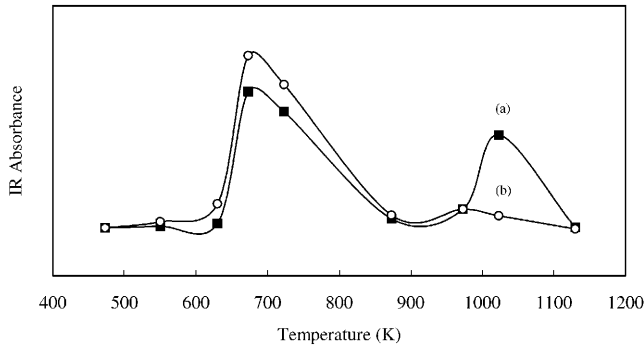


Fig. 3. Temperature dependence for SO₂ emission from oxidation of (a) coarse (30 to 80 mesh) and (b) fine (250 to 300 mesh) resins.

(see Fig. 3) as well as the rapid heat released from oxidation of hydrocarbons in the resin. Note that metal sulfates (e.g., CoSO₄) cannot be decomposed at <1400 K.

The global kinetic parameters (such as the activation energy, reaction order, and preexponential factor) for oxidation of the fine resin were numerically calculated from the TGA weight loss data (with a heating rate of 4, 5, or 8 K·min⁻¹) using the modified Friedman algorithm.¹¹⁻¹⁶ The overall rate equation of conversion factor is expressed in the Arrhenius relation forms:

$$\frac{dx}{dt} = A \exp(-Ea/RT)(1-x)^n [O_2]^m, \quad (1)$$

$$x = \frac{w_0 - w}{w_0 - w_f}, \quad (2)$$

$$k = A \exp(-Ea/RT), \quad (3a)$$

or

$$\ln k = \ln A - Ea/(RT), \quad (3b)$$

where

t = time (s)

A = preexponential factor (s⁻¹)

Ea = activation energy (J·mol⁻¹)

T = reaction temperature (K)

R = universal gas constant (8.314 J·mol⁻¹·K⁻¹)

w = mass of the sample at time t

w_0, w_f = initial and final (or residual) masses of the resin, respectively

x = conversion

n, m = reaction orders for the resin and oxygen, respectively

k = rate constant (s⁻¹).

In Fig. 4, it is clear that oxidation of the fine resin proceeds via two stages (650 to 700 K and 700 to 730 K). In the first stage (650 to 700 K), Fig. 4b shows that the activation energies for oxidation of the fine resin in the presence of 4.2 to 21% of oxygen in nitrogen were 108 to 138 kJ·mol⁻¹. The reaction order for oxygen was approximately 3.5. In the second stage, the activation energies and reaction orders of the resin were 125 to 343 kJ/mol and 0.9 to 2.1, respectively (see Fig. 4c and Table II). The rate equations for oxidation of the resins in the first and second stages can be expressed, respectively, as

$$dx_1/dt = 2.3 \times 10^7 \times \exp(-117900/T)(1-x)^{0.82} [O_2]^{3.5}$$

and

$$dx_2/dt = 8.4 \times 10^{17} \times \exp(-239500/T)(1-x)^{0.9} [O_2]^{4.5}.$$

TABLE I
Weight Losses for Oxidation of Coarse and Fine Resins

	Particle Size (Mesh)		
	30 to 80 (Coarse)		250 to 300 (Fine)
	First Stage	Second Stage	Single Stage
Temperature range (K)	600 to 900	900 to 1173	600 to 900
Total weight loss (%)	29	31	60
Weight loss via decomposition of -SO ₃ H (%)	13	8	20
Weight loss via oxidation of hydrocarbons (%)	16	23	40

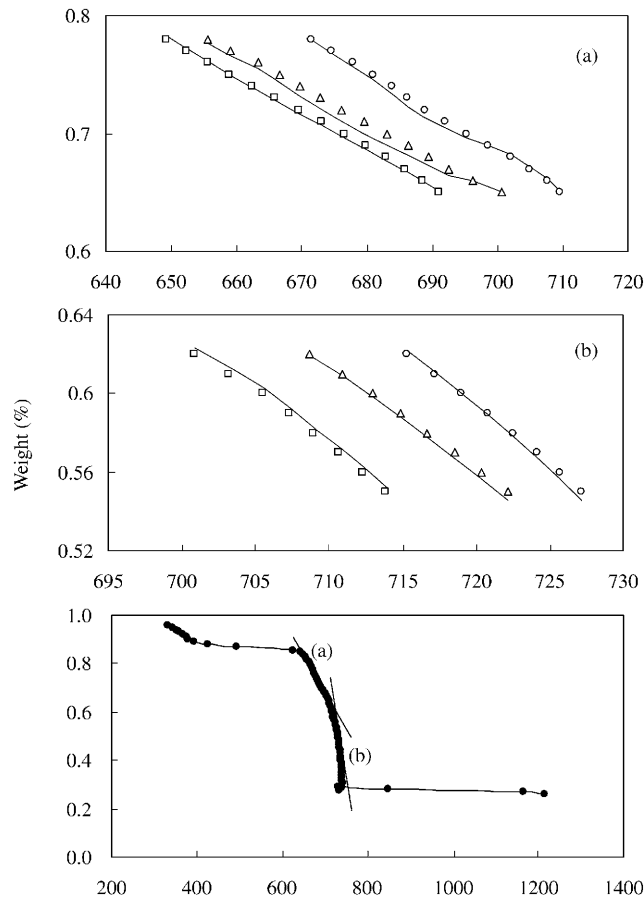


Fig. 4. The Arrhenius plots for oxidation of the fine resin at a heating rate of 4 (\square), 5 (\triangle), or 8 (\circ) K/min in the presence of 21% oxygen in nitrogen. Solid lines denote fits of the oxidation kinetic equations for (a) $dx_1/dt = 2.3 \times 10^7 \exp(-117900/T)(1-x)^{0.82} [O_2]^{3.5}$ and (b) $dx_2/dt = 8.4 \times 10^{17} \exp(-239500/T)(1-x)^{0.9} [O_2]^{4.5}$.

The experimental and predictable data were also examined with the nonparametric Mann-Whitney U tests. Acceptable agreements for the first stage [probability (p) = 0.93, coefficient of determination (r^2) = 0.99] and the second stage (p = 0.75, r^2 = 0.95) were observed. In this study it is suggested these rate equations for oxidation of the resins could be applied to the process of oxidation of spent LLRA resins and with hope, could solve the serious waste problems in nuclear power plants.

IV. CONCLUSIONS

Two-stage reaction was observed in the resin oxidation process. About 29 and 31% of the coarse resin (mainly hydrocarbons) were oxidized at 600 to 900 K and 900 to 1173 K, respectively. Decomposition of SO_4 species in the resin to SO_2 was also formed, which led to a weight

TABLE II

Kinetic Parameters for Oxidation of the Fine Resin*

Oxidant (Percent O_2 in N_2)	Reaction Stage	Ea ($kJ \cdot mol^{-1}$)	n
4.2	First	138	1.00
	Second	343	0.93
12	First	109	0.87
	Second	247	2.10
21	First	108	0.82
	Second	125	0.90

$$*dx_1/dt = 2.3 \times 10^7 \exp(-Ea/T)(1-x)^n [O_2]^{3.5};$$

$$dx_2/dt = 8.4 \times 10^{17} \exp(-Ea/T)(1-x)^n [O_2]^{4.5}.$$

loss of $\sim 21\%$ during oxidation. Enhanced oxidation for the fine resin (minimized perturbation of mass transfer) was observed. The two-stage oxidation rate equations for the fine resin can be expressed as

$$dx_1/dt = 2.3 \times 10^7 \exp(-117900/T)(1-x)^{0.82} [O_2]^{3.5}$$

(650 to 700 K)

and

$$dx_2/dt = 8.4 \times 10^{17} \exp(-239500/T)(1-x)^{0.9} [O_2]^{4.5}$$

(700 to 730 K) .

NOMENCLATURE

- A = preexponential factor (s^{-1})
- Ea = activation energy ($J \cdot mol^{-1}$)
- k = rate constant (s^{-1})
- n = reaction orders for the unreacted resin
- m = reaction orders for the oxygen
- R = universal gas constant ($8.314 J \cdot mol^{-1} \cdot K^{-1}$)
- T = reaction temperature (K)
- t = time (s)
- w = mass of the sample at time t
- w_0 = initial masses of the resin
- w_f = final (or residual) masses of the resin
- x = conversion

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