

Trial Destruction Test of Spent Cationic Resins in a Molten Salt Oxidation Reactor System

Hee-Chul Yang*, Yong-Jun Cho, Hee-Chul Eun, Soon-Jae Hong, Kune-Woo Lee
Korea Atomic Energy Research Insitutue, Dukjindong 150, Yuseong, Daejeon, 305-353, Korea
*Corresponding author:nhcyang@kaeri.re.kr

1. Introduction

The spent ion-exchange resins have to be disposed of and as such, spent ion-exchange resins are a significant fraction of the combustible organic waste from the nuclear industries. One effective treatment option is incinerating the spent resins to yield ash and gas. However, there are difficulties associated with this approach. One of the criticisms of a high-temperature incinerator is that radioactive and hazardous metals are not retained in the incinerator. In addition, incineration of the cationic exchange resins, which have the sulphur-containing functional groups of sulfonic acid ($-\text{SO}_3-\text{H}^+$), has revealed significant problems associated with sulfur dioxide (SO_2), a primary air pollutant, which must be kept under control [1]. There is therefore the developing need for an alternative destruction process. Molten salt oxidation, or MSO for short, is a promising alternative technology. Molten carbonate filled in a MSO reactor is capable of trapping sulfur during organic destruction [2,3]. In addition, the relatively low-operation temperature of the MSO reactor reduces the volatility of the radionuclides, compared to the other available high-temperature technologies for organics destruction, such as inductively coupled plasma, incineration, plasma arc and microwave heating [4].

Trial destruction tests of spent cationic exchange resins doped with radioactive metal surrogates were performed in this study. Two typical operating parameters, temperature and oxidizing air rate, which significantly affect the organics destruction, were tested to establish the optimum ranges for those parameters.

2. Methods and Results

2.1 Trial Destruction Methods

A binary carbonate salt mixture, which consisted of 44 mol% K_2CO_3 and 56 mol% Na_2CO_3 , was used as a molten salt. The eutectic temperature of the used binary salt mixture is 710°C. The selected commercial cationic exchange resins used in this study are Amberlite IRN-77, which have the structure of a styrene-divinylbenzene (ST-DVB) copolymer styrene with a functional group of $-\text{SO}_3-\text{H}^+$ [5]. In this study, the count ion H^+ is exchanged for Co^{+2} , Sr^{+2} and Cs^{+1} with an aqueous solution containing those ions of radioactive metal surrogates. Prepared waste spent resins were dried at 150°C for 3 hours. The compositions of the dried spent

resins and concentration of fixed radioactive metal surrogates are shown in Table 1.

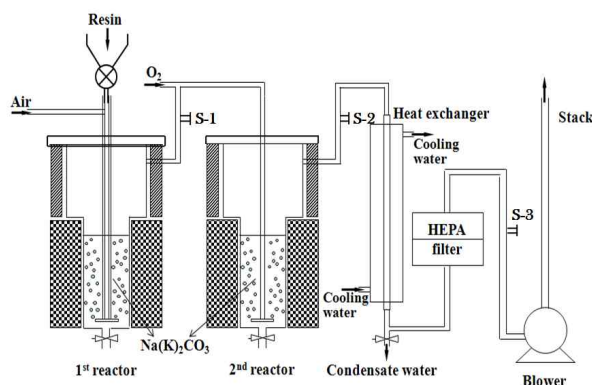


Fig. 1. A schematic of bench-scale MSO system

Table 1. Compositions of Tested Cationic Exchange Resins

Proximate analysis, dry(wt%)	Volatile matter		Fixed carbon			Ash	
		43.35		41.28			15.37
Ultimate analysis (wt%)	C	H	O	S	Co	Cs	Sr
	40.5	3.1	28.4	11.5	3.93	3.75	2.01

2.2 Organics Destruction

The typical emission concentrations of hydrocarbons measured by GC/MS analysis of off-gas samples are shown in Table 3. During the worst-case condition for organics destruction (lowest temperature and oxidizing air rate), a significant amount of methane, diacetamide and benzene was released. Due to this considerable amount of volatile content, a significant amount of volatile organics are suddenly released after feeding of spent resins into the hot molten salt. Suddenly released hydrocarbons are not substantially destroyed at 750°C and under the excess air rate of 50%. An enhanced oxidizing condition with increasing temperature and oxidizing air rate could effectively destroy hydrocarbons released from ion-exchange resin particles. An acceptable organics destruction performance was obtained at the reactor temperature of 850°C and excess air rate of 100%. At this condition, the total emissions of hydrocarbons could be limited to below 1 ppm at 850°C and 100% excess air.

Table 3. Hydrocarbon emissions during cationic ion-exchange resin destruction tests

Hydrocarbon species	750°C, φ=1.5	850°C, φ=1.5	850°C, φ=2.0
Methane	77.62	6.76	0.40
Diacetamide	24.44	1.44	0.01
Benzene	13.26	1.40	ND
Toluene	1.82	0.09	ND
MEK	0.85	0.05	ND
1-Propynyl benzene	0.62	0.03	ND
m,p-Xylene	0.48	0.03	ND
Styrene	0.34	0.02	ND
Others	0.25	0.01	ND
sum	119.69	9.84	0.41

This excellent organic destruction performance of the MSO reactor can be explained by the excellent mixing compared to incinerator. In a molten salt reactor, the oxidizing air flows turbulently upward through a large bed of molten salt. Therefore, molten salt reactor has an excellent mixing capacity like a bubble column reactor or a fluidized bed reactor. The temperatures and heat transfer are also completely uniform within the molten salt bed and no dead zone exists unlike a fixed-bed incinerator.

Emissions of carbon monoxides are shown in Fig. 2. The emissions of CO were greatly influenced by the excess air rate. Not less than a thousand ppm of CO was emitted under the conditions of excess air rate of 50%, regardless of the tested temperature up to 950°C. The influence of temperature on the CO emission was also considerable but relatively smaller, when compared to that of excess air rate. The emissions of CO appeared to be stable under at the temperature 850°C or higher and under the excess air rate of 100% or higher. Emissions of other hazardous gases such as NO_x and SO₂ were relatively very low. The emissions of NO_x did not exceed 30 ppm even under the highest-temperature test at 950°C. This is because of both the limited local temperatures due to a non-flame oxidation as well as the absence of source of fuel NO_x in the resins. The emissions of SO₂ did not exceed 1 ppm, although a significant amount SO₂ released from the destruction of cationic resins. For the tested cationic exchange resins, which include about 11.5% sulfur by mass as shown in Table 1, the maximum SO₂ emission did not exceed 3 ppm throughout all the tests. This suggests that the following SO₂-capturing reaction nearly complete in the alkaline molten salt.

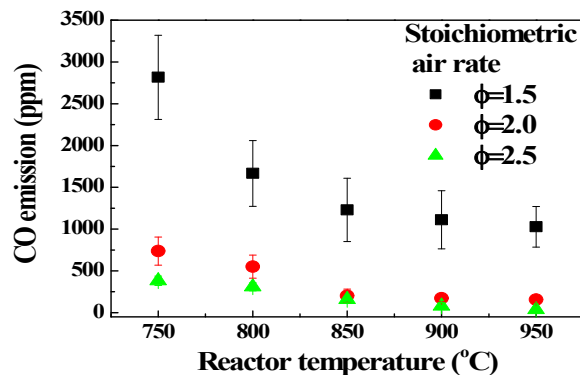
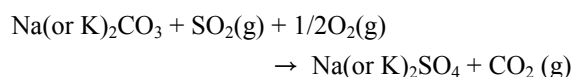


Fig. 2. Carbon monoxide emission of CO as a function of MSO reactor temperature

3. Conclusions

The optimum operating condition for the destruction of cationic exchange resins was determined to be the temperature of 850-900°C and the excess air ratio of 100-150%. In these conditions, the emissions of carbon monoxide as well as THCs were effectively controlled within the regulatory limit. In addition, no significant emissions of NO_x and SO₂ were found throughout all the test runs.

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