

Optimization of a Molten Carbonate Reactor System for a Destruction of Spent Cationic Ion-exchange Resins

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Optimum operating conditions of a molten carbonate reactor system for a destruction of spent cationic ion-exchange resins were determined based on the characteristics of hazardous gas emissions such as THCs and CO and the behavior of radioactive metals such as cobalt, cesium and strontium. The organic destruction performance was tested by changing the reactor temperature from 750°C to 950 °C and the excess air rate from 50 % to 150 %. Optimum conditions for organics destruction were determined to be the excess air ratio of 100-150 % and the reactor temperature of 850-900 °C, respectively. A further increase in the reactor temperature resulted in a greater emission of cesium species.

1. Introduction

Ion-exchange resins are polymer granules that are capable of exchanging some of their constitutive ions with other ions in a solution that is passing through them (Antoneti et al., 2000). Commercial nuclear industries utilize ion-exchange resins to clarify their process and process water. The resins are used to remove unwanted impurities such as radioactive, hazardous, or other contaminants that could potentially harm the equipment or corrode the nuclear reactor fuel rods. The spent ion-exchange resins have to be disposed of and as such, spent ion-exchange resins are a major fraction of the combustible organic waste from the nuclear industries (Cicero-Herman, 1998). 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 sulphuric acid ($-\text{SO}_3\text{-H}^+$), has revealed significant problems associated with sulphur dioxide (SO_2), a primary air pollutant, which must be kept under control (Li et al., 1994).

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 sulphur during organic destruction (Hsu et. al., 2000 and Yang et al., 2005). 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 (Nezu et al. 2003). This study investigated the optimum condition of a bench-scale MSO for the treatment of spent cationic exchange resins.

2. Experimental Method and Analysis

2.1 MSO reactor system

The schematic diagram of a bench-scale MSO system is shown in Fig. 1. The system consists of a MSO reactor system, an off-gas treatment system and an off-gas analysis system. The MSO reactor system consists of two identical MSO reactors and an off-gas treatment system. The top of the primary MSO reactor cover is connected with a rotary feeder for feeding spherical ion-exchange resins 0.5 to 1 mm in diameter. Fed resins fall down to the bottom of the MSO reactor through a 0.025 m vertical tube, along with the oxidizing air. An off-gas exhausting pipe, positioned directly underneath the primary MSO reactor cover, is connected to a secondary MSO reactor, which has the functions of collecting the entrained salt particles and oxidizing the unburned hydrocarbons and carbon monoxide in the off-gas leaving the primary MSO reactor. The pure oxygen-supplying system is connected to the outlet of the primary reactor so that supplied pure oxygen can enhance the oxidation efficiency of secondary reactor. The off-gas treatment system includes a condenser, a filter and a heat exchanger. The off-gas leaving the secondary MSO reactor is cooled down to about 200°C by a vertical water-to-gas heat-exchanging condenser. A high-efficiency particulate air (HEPA) filter filters the off-gas leaving the heat exchanger.

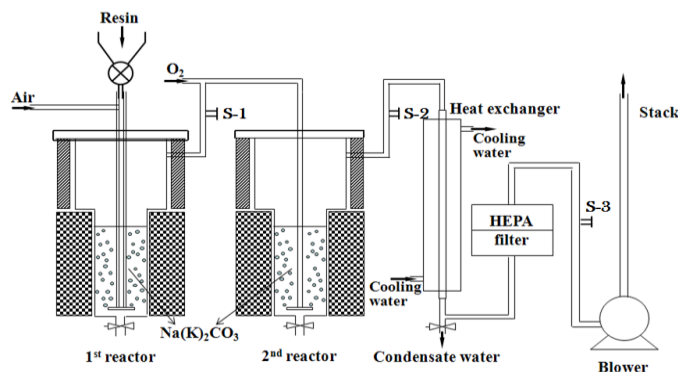


Figure 1: A schematic diagram of bench-scale MWO reactor system

2.2 Materials and 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 (Janz, 1967). 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 $-SO_3-H^+$ (Antoneti et al., 2000). 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 h. The compositions of the dried

spent resins of this study are shown in Table 1. Volatile, fixed carbon and ash contents of the prepared spent resins are analyzed to be 43.35, 41.28 and 15.37 %, respectively. The results of ultimate analysis and concentration of fixed radioactive metal surrogates are also shown in Table 1.

Table 1 Compositions of dried spent cationic exchange resins used in this study

<i>Proximate analysis</i> (wt%)	<i>Moisture</i>	<i>Volatile matter</i>	<i>Fixed carbon</i>	<i>Ash</i>
	-	43.35	41.28	15.37
<i>Ultimate analysis</i> (wt%)	<i>C</i>	<i>H</i>	<i>O</i>	<i>S</i>
	40.50	3.1	28.4	11.5
<i>Radioactive metal surrogate</i> (wt%)	<i>Co</i>	<i>Cs</i>	<i>Sr</i>	<i>others</i>
	3.93	3.75	2.01	-

2.3 Test methods and analysis

Preliminary tests were performed to determine an appropriate salt level and oxidizing air feed rate, which provides neither significant entrainment of salt particles nor significant pressure drop during air bubbling from the bottom of the molten salt. Through the entire tests the salt levels (L/D) in the two cylindrical MSO reactors were fixed to be 2.5, where L and D represent a salt bed height and a reactor inner diameter, respectively. MSO reactor test programs for the destruction of spent cationic ion exchange resins are summarized in Table 2. Test variables were the primary reactor temperature and the stoichiometric air rate. Secondary reactor temperature was fixed to be 850°C. The performance of organic destruction and the emissions of hazardous gases were first investigated by varying test variables. A total of 15 test runs were performed by changing excess air rate as 50, 100 and 150 % for each of five different reactor operating temperatures of 750, 800, 850, 900 and 950 °C. Off-gas sampling locations are indicated as S-1, S-2 and S-3 in Figure 1.

Table 2 Test conditions to determine optimum operating conditions

Test No.	Excess air rate (%)	Primary Reactor Temp. (°C)	Sampling location	Measurement	Optimizing parameters
T1-T5	50 %	750, 800, 850, 900, 950	S-3	Emissions of CO, NO _x , SO ₂ , HCs (T1, T3, T6)	Temperature and oxidizing air rate
T6-T10	100				
T11-T15	150				
T16	100	850	S-1, S-2 and S-3	Partitioning of radionuclide	Allowable feed amount
T17	100	950			

During the first serious test runs (T1-T15) the emissions of the hazardous gases such as CO, NO_x and SO₂ were continuously measured at the sampling location of S-3 by using a combustion efficiency analyzer (TESTO-350). The emissions of hydrocarbons were measured by the GC/MS (gas chromatography and mass spectrometer) analysis of sampled off-gas in the Teflon sample bags during the tests of T1, T3 and T6. Three sets of particulate air sampling train were installed for radioactive metal partitioning test (T16 and T17) at the sampling locations of S-1, S-2 and S-3. The total amount of the

entrained particle concentration in each flue gas stream was determined by the weight difference of the sampling filter before and after particulate sampling. After weighing, the sampling filter was dissolved in aqua regia (HNO_3 : HCl : H_2O = 1:3:1) at 100 °C. The solution was then diluted by boric acidic solution. Concentrations of each metal species in the acid solution were measured by the ICP-MS (Inductively coupled plasma – mass spectrometer).

3. Results and Discussion

3.1 Organic Destruction

The typical emission concentrations of hydrocarbons measured by GC/MS analysis of off-gas samples are shown in Table 3. During T1 test, which could be regarded as the worst-case condition for organics destruction, a significant amount of methane, diacetamide and benzene was released. Used spent cationic exchange resins have the structure of a styrene-divinylbenzene (ST-DVB) copolymer styrene. As shown in Table 1, the volatile content of dried resin is 43.35 %. 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 T1, T3 and T6 tests

Hydrocarbon species	T1 (750 °C, 50% excess air)	T3 (T=850 °C, 50% excess air)	T6 (850 °C, 100% excess air)
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 % sulphur 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.

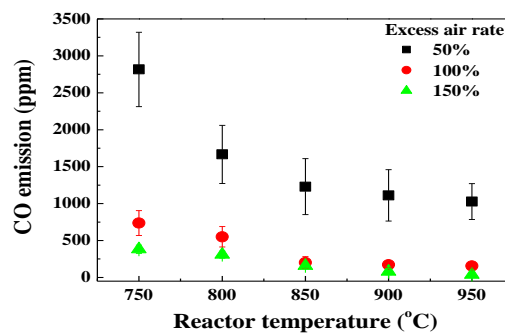
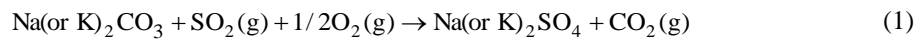


Figure 2: Emissions of carbon monoxides as a function of MSO reactor temperature and excess air rate

3.2 Partitioning of Radioactive Metals

Based on the analyzed metal concentration at each sampling location (S-1, S-2 and S-3 in Fig 1), the overall partitioning of the radioactive metal surrogates in different secondary waste steams was calculated to be 100% by using following equations.

$$M_{MS1} = M_T - M_{S-1}, M_{MS2} = M_{S-1} - M_{S-2}, M_{HF} = M_{S-2} - M_{S-3} \quad (2)$$

where M_T is the total mass of the fed metal, M_{MS1} , M_{MS2} and M_{HF} are the quantities of metals remaining in the primary reactor, those remaining in the secondary reactor and HEPA filter, respectively.

Results of metals partitioning are shown in Table 4. Most of the cobalt and strontium partitioned into the molten salt and the minor fraction entrained was efficiently collected in the HEPA filter. Cobalt might convert to form a stable oxide (CoO and Co₂O₃) in the presence of oxygen and strontium also might convert to form non-volatile oxide such as SrO and SrCO₃ in molten carbonate. It is therefore suggested that the entrained cobalt and strontium was the particulate entrainment along with entrained molten salt particles. The partitioning of cesium varied noticeably with the tested temperature. About 90% of cesium remained in the molten salt at 850 °C. However, a half of cesium entrained into off-gas at 950 °C and its final emission was also considerable. It was suggested that a certain fraction of cesium converted to from volatile its oxide (Cs₂O), while remaining fraction of cesium converted to form non-volatile carbonate (Cs₂CO₃) or surfate (Cs₂SO₄). Volatilised cesium species may condenses out into particles to form submicron particles and thus the collection of those

particles though HEPA filter system was not substantial. This may results in the emission of a significant amount of cesium during 950 °C tests. It is therefore concluded that the optimum operating condition of MSO reactor system is 850 °C and excess air rate of 100 %.

Table 4 Partitioning (%) of radioactive metal surrogates at excess air rate of 100%

	Co		Sr		Cs	
	850°C	950°C	850°C	950°C	850°C	950°C
1 st Reactor	96.6E-01	9.85E-01	9.23E-01	9.63E-01	8.92E-01	4.74E-01
2 nd Reactor	3.31E-02	1.36E-02	7.36E-02	3.50E-02	9.19E-02	1.50E-01
HEPA Filter	1.38E-03	1.36E-03	3.34E-03	1.94E-03	1.56E-02	3.96E-01
Emission	1.15E-08	1.94E-08	5.87E-08	3.66E-08	6.49E-07	4.27E-05

4. Conclusions

The organic destruction performance was greatly enhanced by increasing reactor temperature or excess air rate. However, too much increase in the temperature resulted in a significant amount of cesium volatilization in the flue gas. Therefore optimum conditions for the destruction cationic spent resins were determined to be the excess air ratio of 100-150 % and the reactor temperature of 850-900 °C, respectively.

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