

Explosion hazards of ion exchange resin mixed with perchloric acid

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Abstract On January 21, 2003, an explosion occurred while ion exchange resin (IER) was being used to separate impurities from uranium solution. To clarify the cause of the accident and go/no-go criteria of the explosion, elemental analysis of the IER, DSC analysis, and SIKAREX analysis (a screening tool for runaway reactions) were performed. Finally, experiments on the same scale as the accident were conducted in an explosion chamber. When HClO_4 was added to IER- NO_3 , the IER violently exploded without any heating nor metal ions such as uranium. It was confirmed that the accident was caused by an incorrect procedure in the chemical process. From the standpoint of explosion safety, IER- NO_3 in particular should be kept away from perchloric acid in the laboratory.

Keywords Ion exchange resin · Accident analysis · Perchloric acid

Introduction

On January 21, 2003, an explosion accident occurred in which an ion exchange column exploded and a worker was injured by glass fragments at the Ningyo-toge Environmental Engineering Center of the Japan Atomic Energy Agency (JAEA). The accident took place during the isotopic analysis of depleted uranium using a mass spectrometer, which requires the removal of impurities from a uranium solution using an ion exchange process in the laboratory. After the ion exchange process, the eluted solution is mixed with 12N (70 mass%) perchloric acid (HClO_4) to decompose the organic compounds. This accident was caused by the use of an incorrect procedure in the chemical process, when the worker concerned added HClO_4 to the ion exchange resin (IER) in the glass column by mistake. Explosion accident reactions between nitric acid and IER are known to have occurred [1, 2] (Fig. 1). As nitric acid and organic materials are generally used in nuclear reprocessing, it is necessary to pay attention to the possibility of a reaction between them.

In the present study, we conducted differential scanning calorimetry (DSC) analysis and gram-scale thermal analysis (SIKAREX analysis) of mixed samples of IER- NO_3 / HClO_4 . Burnham et al. [3] showed that kinetics from DSC sometimes simulate large-scale experiments well and sometimes not. To investigate the explosion phenomena, reproducible experiments of the explosion accident were conducted in an explosion chamber.

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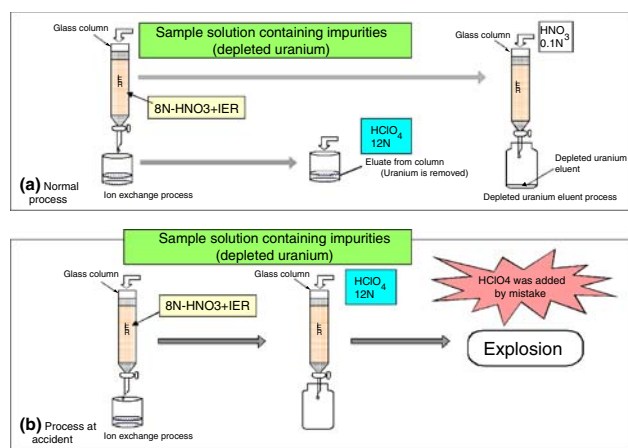


Fig. 1 Ion exchange process to remove impurities using IER: **a** normal process **b** process at time of accident

Experimental procedure

Preparation of IER

AG1-X8 (Bio-rad, 100–200 mesh) 8% cross-linked resin is a strongly basic anion exchanger with quaternary ammonium functional groups attached to a styrene divinylbenzene copolymer lattice. The active group is $R-CH_2N^+(CH_3)_3$ (Fig. 2). AG1 resin is supplied in the chloride form. A Cl^- type IER sample was used as the dried supplied sample. The NO_3^- type IER sample (IER- NO_3) was prepared as follows. To convert AG1-X8 resin from the Cl^- form to the OH^- form, a 4–5 bed volume of 1N-NaOH was added to the IER. The IER was then converted from the OH^- form to the NO_3^- form using a 4–5 bed volume of 1N- HNO_3 . Finally, the NO_3^- form resin was washed with water and dried under a vacuum. IER- ClO_4 and IER- Cl were prepared using 1N- $HClO_4$ and 1N- HCl , respectively.

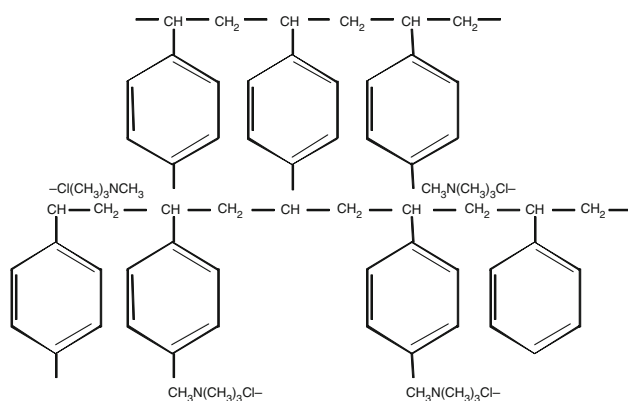


Fig. 2 Chemical structure of IER-Cl (AG1-X8, Bio-rad)

Elemental analysis and heat of combustion analysis

Elemental analyses for C, H, N, and O were performed on an elemental analyzer (CE Instruments EA1110, EA1112). The amount of Cl was determined by gravimetric analysis of the precipitation of $AgCl$. Oxygen balance (OB) is generally used in the evaluation of explosives. Using the element ratio of C/H/N/O/Cl, OB is calculated. OB indicates the degree to which an explosive can be oxidized. As the OB approaches zero, the sensitivity and strength of an explosive tend toward their maximum values. A bomb calorimeter (C2000 basic, IKA) was used to measure the heat of combustion of the IER. After standardization with benzoic acid, 1 g samples of IER enclosed in gelatin capsules were burned in the bomb. Measurements were repeated three times.

Sealed cell differential scanning calorimetry (SC-DSC) analysis

SC-DSC measurements were performed using a DSC2920 model (TA Instruments). The samples of IER ranged in amount from 1 to 2 mg. The heating rate was 5 K/min. Measurements were conducted from room temperature (RT) to 500 °C under a 3 MPa N_2 condition. The sealed cell was a Netzsch high-pressure vessel (up to 15 MPa) (Hastelloy).

SIKAREX analysis

A SIKAREX (SYSTAG) system was used to investigate the gram-scale thermal reaction. The SIKAREX system can be used for the screening of large amounts of samples under close to actual process conditions [4] (Fig. 3). Adiabatic heating experiments on samples of up to 8–10 g are available in this system, compared with about 1 g in the case of an accelerated rate calorimetry (ARC) system. The

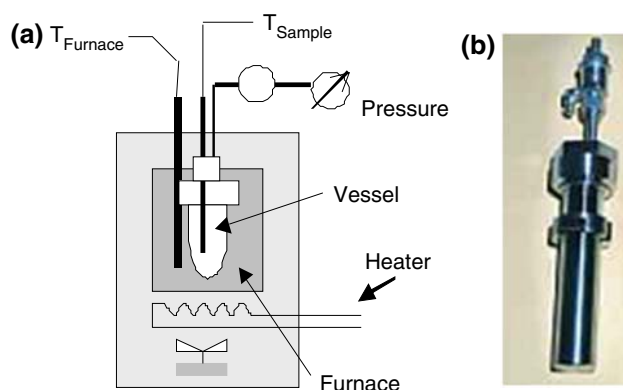


Fig. 3 **a** Schematic diagram of SIKAREX furnace, and **b** photograph of outer stainless steel vessel

sample vessel has a double-shell structure with a 15 MPa bursting disk. The inner vessel is made of glass (50 mL, 20 mm dia × 120 mm L) and the outer vessel is made of stainless steel. The outer vessel is not broken by a strong explosion. There are two thermocouples (T_{Furnace} and T_{Sample}), located in the furnace and the sample, respectively. Exothermic data from the sample were detected by T_{Sample} . The heating rates of the furnace in the present study were 0.5 K/min and 3.0 K/min up to 300 °C. The samples consisted of (a) IER-NO₃ 5 g/8N-HClO₄ 1 mL and (b) IER-NO₃ 5 g/8N-HClO₄ 5 mL.

Gram-scale explosion tests in explosion chamber

To investigate the hazard reaction between IER and HClO₄, gram-scale explosion tests were conducted in an explosion chamber (2.9 m diameter, 3.45 m H). HClO₄ was remotely added to the IER samples using a long pole with tongs. Three types of tests were conducted with various sample masses, using a glass test tube or glass column with the following inside diameter (ID):

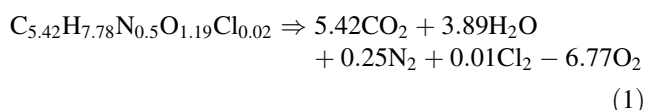
Tests #1-1 to 1-9	IER 5 g	ID = 15 mm, glass test tube
Tests #2-1 to 2-9	IER 10 g	ID = 27 mm, glass test tube
Tests #3-1 to 3-4	IER 20 g	ID = 20 mm, L = 30 mm, glass column

In these tests, polytetrafluoroethylene (PTFE)-covered thermocouples (K-type, Chino) were used for temperature measurement and video recording was conducted. Four types of temperature measurements were performed: sample temperatures 1 and 2, the outer part of the glass tube, and RT. We mainly focused on the adiabatic effect, the effect of the metal catalyst, and the scale effect. Uranyl ion, which behaves as a positive catalyst, was used at the time of the accident. Since we could not use radioactive materials in our explosion experiments, the alternative chemical reagents K₂Cr₂O₇, K₂CrO₄, and Bi(NO₃)₃ · 5H₂O were selected as positive catalysts instead. After HClO₄ was added to the IER, the temperature increased. If the temperature decreased, the glass tube was heated by a ribbon heater or heating gun to terminate the experiment safely.

Results and discussion

Fundamental analysis of IER

Table 1 shows the C/H/N/O/Cl mol ratio of IER-Cl, IER-NO₃, and IER-ClO₄. Although the IER had been dried under a vacuum condition, it was found that water remained. The OB of all of the IER samples was −200, which is far from zero. The complete combustion equation is shown below. The IER itself does not have a serious explosion hazard.



DSC analysis

In the case of IER-NO₃ (Fig. 4a) there was a small and broad exothermic reaction at around 224 °C (T_a). When HClO₄ was added to the IER, the thermal behavior drastically changed (Fig. 4b, c). Small-scale, slow exothermal behavior was seen under 100 °C, then a large, two-step exothermal reaction occurred above 200 °C. The exothermic onset temperature was T_{a1} and T_{a2} , respectively. When the concentration of added HClO₄ was increased, T_{a2} decreased (from 206 to 183 °C) and Q_{DSC} (the heat of decomposition) increased (from 2,100 J/g to 2,930 J/g), indicating an oxidation-reduction reaction between the organic material (IER) and HClO₄. From these results, it was found that the mixture of IER-NO₃ and HClO₄ has a large exothermal reaction. However, it was not possible to determine whether an explosion would occur by means of this mg-scale thermal analysis. Larger scale experiments, namely, SIKAREX analysis and gram-scale explosion tests, were therefore conducted.

SIKAREX analysis

Figure 5a shows the temperature profile of SIKAREX analysis. There was an endothermic reaction from 100 °C, and the sample strongly exploded at 167 °C. The sample temperature drastically increased at this point, which we refer to as the self-ignition temperature (SIT). The SITs shown in Fig. 5b-1 and b-2 were 215 °C and 167 °C,

Table 1 Fundamental analysis of IER (C/H/N/O/Cl ratio and heat of combustion)

	C (mol)	H (mol)	N (mol)	O (mol)	Cl (mol)	OB	Heat of combustion (kJ/g)
IER-Cl	4.66	8.71	0.21	1.42	0.27	−194	−
IER-NO ₃	5.42	7.78	0.51	1.19	0.02	−217	29.7
IER-ClO ₄	5.04	8.24	0.36	1.31	0.15	−193	−

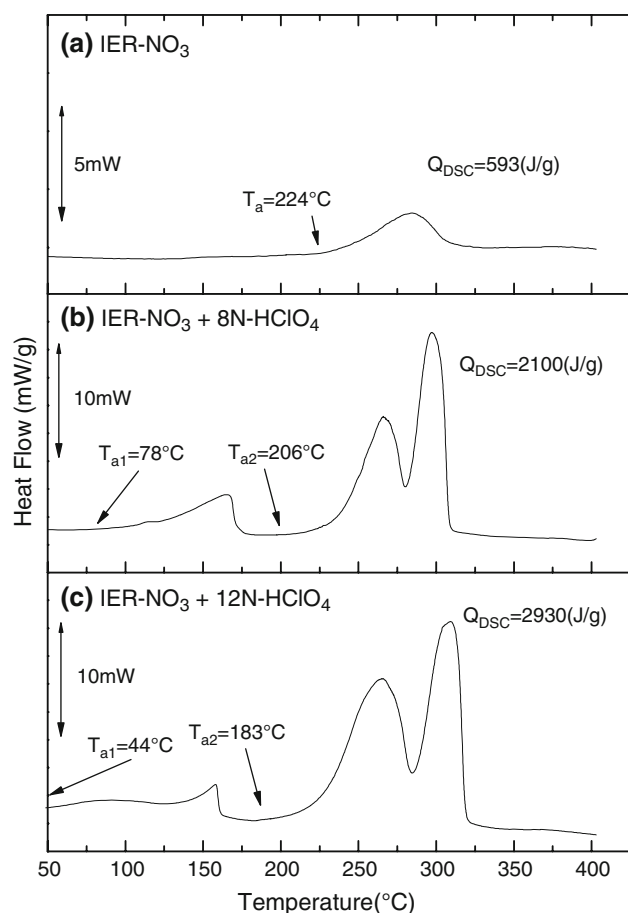


Fig. 4 DSC profiles of **a** IER-NO₃, **b** IER-NO₃ + 8N-HClO₄, and **c** IER-NO₃ + 12N-HClO₄

respectively. The temperature difference between T_{Furnace} and T_{Sample} reached 60 °C in the test results shown in Fig. 5b-1. In this test the glass vessel was not broken, but because of the strong reaction there was no residue. On the other hand, in the test results shown in Fig. 5b-2, the glass vessel and rupture disk were broken and the outer stainless steel vessel was deformed due to the violence of the explosion. It was not possible to continue further experiments because of the deformation of the stainless steel vessel. The results of the SIKAREX analysis demonstrated that the SIT and strength of the explosion are strongly dependent on the amount of added 8N-HClO₄.

Gram-scale explosion tests

Table 2 shows a summary of the gram-scale explosion tests. In tests #1-1 to 1-9, a 15 mm diameter glass tube was used with 5 g of IER and 5 or 10 g of 12N-HClO₄. There was no combustion or explosion without the application of heat. The use of additive salts (#1-3, 1-6, 1-8, and 1-9) produced no significant effect. In tests #2-1 to 2-9, a 27 mm glass tube was used with 10 g of IER and 20 g of

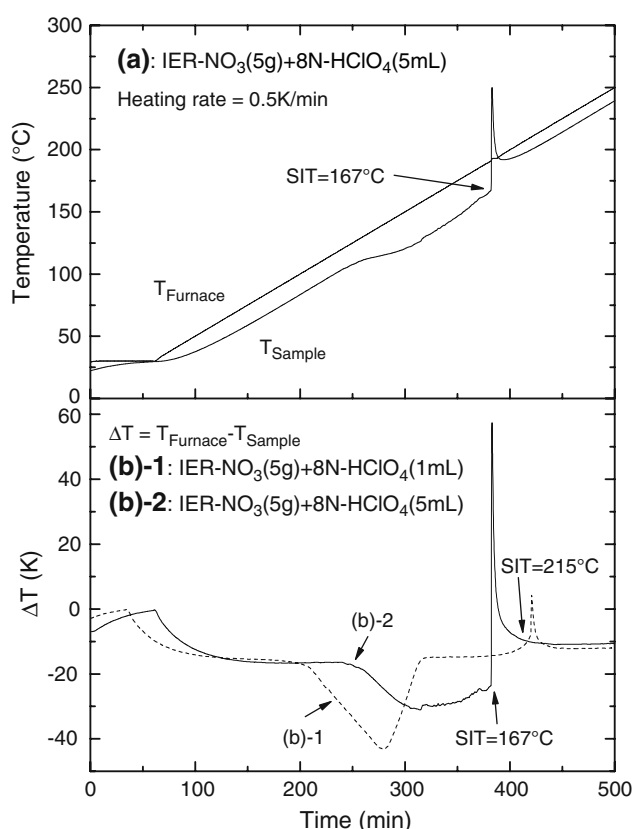


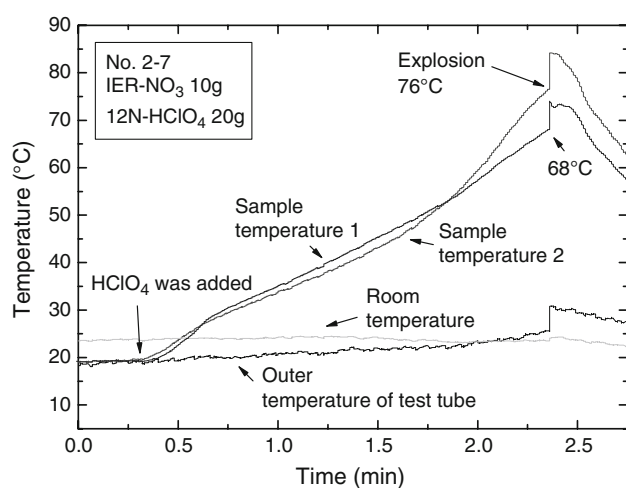
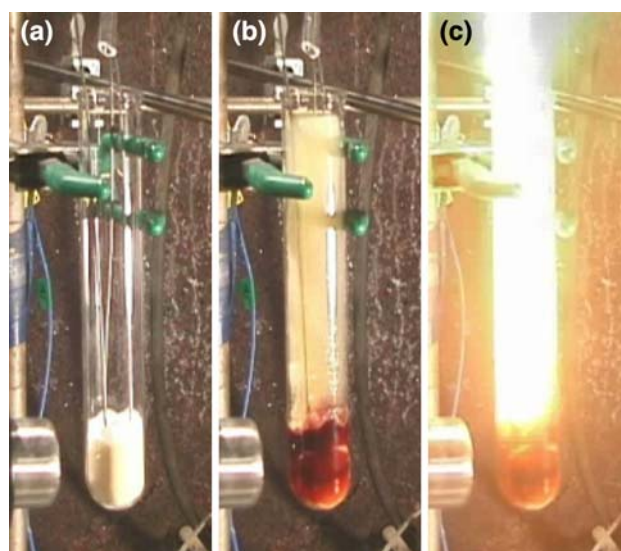
Fig. 5 Results of SIKAREX analysis: **a** temperature profile of IER-NO₃ (5 g) + 8 N-HClO₄ (5 mL), **b** $T_{\text{Furnace}} - T_{\text{Sample}}$ profiles of **b**-1 IER-NO₃ (5 g) + 8N-HClO₄ (1 mL) and **b**-2 IER-NO₃ (5 g) + 8N-HClO₄ (5 mL)

12N-HClO₄. There was some combustion or explosion (#2-1, 2-2, and 2-5 to 2-8) without heating. The heat of reaction was accumulated. The gradual increase in the sample temperature led to explosion. Figure 6 shows the temperature profile of test #2-7 (IER-NO₃ 10 g + 12N-HClO₄ 20 g). The temperature gradually increased from RT to 68–76 °C without the application of heat. In the case of tests #2-1, 2-2, 2-5 to 2-8, 3-3, and 3-4, combustion or explosion occurred without the application of heat. Figure 7 shows photographs of the #2-7 gram-scale explosion test. With the addition of HClO₄ to the IER, the color of the IER changed from white to dark red. There was some gas generation, as seen in Fig. 7b. Gas analysis was not conducted. As the color of the gas was dark red, the generated gas may have consisted of Cl_x and NO_x from the decomposition of HNO₃ and HClO₄.

Figure 7c shows the ignition and explosion of the IER. The glass tube was completely fragmented after the explosion. In the ion exchange process at the time of the actual accident, the top of the IER was covered with glass wool. The time to combustion in test #2-1 was 9.6 min, while that in test #2-5 was 2.3 min. The difference between

Table 2 Gram-scale explosion tests

Shot No.	IER Type	IER (g)	HClO ₄ (g)	HNO ₃ (g)	Additive salt	Outer insulator	Upper insulator	Heating method	Combustion/explosion	SIT (°C)	Time to ignition (min)
#1-1	NO ₃	5	5	5	–	No	No	Ribbon heater	Exp.	132	
#1-2				–					Exp.	101	
#1-3					K ₂ CrO ₄ (1 g)				Exp.	122	
#1-4			10		–				Exp.	125	
#1-5									Exp.	110	
#1-6					Bi(NO ₃) ₃ · 5H ₂ O (1 g)				Comb.	177	
#1-7					–	Yes			Exp.	183	
#1-8					Bi(NO ₃) ₃ · 5H ₂ O (1 g)				Exp.	–	
#1-9					K ₂ Cr ₂ O ₇ (1 g)				Exp.	131	
#2-1	NO ₃	10	20	–	–	Yes	No	–	Comb.	147	9.6
#2-2					Bi(NO ₃) ₃ · 5H ₂ O (1 g)				Exp.	142	6.7
#2-3					K ₂ Cr ₂ O ₇ (1 g)			Ribbon heater	Exp.	198	
#2-4				5	–				Exp.	165	
#2-5				–			Yes	–	Comb.	143	2.3
#2-6					Bi(NO ₃) ₃ · 5H ₂ O (1 g)				Comb.	90	1.6
#2-7					–	No			Exp.	76	2.3
#2-8										158	1.7
#2-9	Cl							Heating gun	Exp.	62	
#3-1	NO ₃	20	5	13	–	No	Yes	Heating gun	Exp.	143	
#3-2			10						Comb.	8	
#3-3								–	Exp.	35	1.3
#3-4			20						Exp.	130	2.2

**Fig. 6** Temperature profile of #2-7 gram-scale test (IER-NO₃ 10 g + 12N-HClO₄ 20 g)**Fig. 7** Photographs of #2-7 gram-scale test (IER-NO₃ 10 g + 12N-HClO₄ 20 g): **a** t = 0 s, 20 °C; **b** t = 120 s, 70 °C; **c** t = 130 s, 85 °C

tests #2-1 and 2-5 was the absence or presence, respectively, of an upper insulator. The adiabatic effect of glass wool on the upper part of the IER is large. In the tests using a 20 mm-diameter glass column (#3-1 to 3-4), there was no ignition in the case of tests #3-1 (12N-HClO₄ 5 g) and 3-2 (12N-HClO₄ 10 g), in which heat was applied. On the other hand, explosion occurred in tests #3-3 (12N-HClO₄ 10 g) and 3-4 (12N-HClO₄ 20 g), in which there was no application of heat. In this system, therefore, the go/no-go criterion is dependent on the amount of HClO₄.

It is known that aqueous HClO₄ has limited use in catalyzing HNO₃ nitration. A disadvantage is the increasing danger of explosion accompanying the use of HClO₄ in concentrations greater than 72 mass%. A mixture of HNO₃-HClO₄ generates nitronium perchlorate (NP, NO₂ClO₄). NP rapidly interacts (frequently with self-ignition) at RT with almost all organic compounds. Perchloric acid in the absence of sufficient water is a very powerful oxidizing agent and a potent dehydrating agent [5–7]. In the present study, it is possible that two types of explosive compounds were generated in the mixtures of IER/HNO₃/HClO₄; namely, nitro-aromatic compounds produced from the styrene divinylbenzene of the IER, and NP generated from the mixture of HNO₃ and HClO₄.

Conclusions

As the OB calculated from the C/H/N/O/Cl ratio of IER-NO₃ is -217, IER-NO₃ itself does not have an explosion

hazard. In the DSC and SIKAREX analysis, the mixture of IER-NO₃ + HClO₄ showed a large exothermic reaction and violent explosion, respectively. In the gram-scale explosion tests, combustion or explosion occurred in the case of most of the samples (IER-NO₃ 20 g + 12N-HClO₄ 10–20 g) without the application of heat and without uranium ion. It has therefore been confirmed that the accident was caused by the use of an incorrect procedure for the chemical process. From the viewpoint of explosion safety, IER-NO₃ in particular should be kept away from perchloric acid.

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