

Iodine Removal from CsI by FeCl_2 -Assisted Air Oxidation

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Abstract

CsI was used as a surrogate to investigate the removal of iodine from spent nuclear fuel. The effects of the oxidizing atmosphere and auxiliary reagent on the oxidative volatilization of iodine from CsI were investigated. The results showed that when CsI was directly oxidized by 7% ozone or O_2 , only a small fraction of CsI was converted to cesium iodate, and iodine could not be removed effectively. The iodine removal efficiency improved significantly after the addition of $FeCl_2$, and similar iodine removal efficiencies were obtained under air, 7% ozone, and O_2 . This indicates that $FeCl_2$ plays a key role in promoting the reaction, and air is sufficient as the reaction atmosphere for iodine removal. On this basis, air was used as the oxidizing atmosphere to further investigate the effects of reaction time, $FeCl_2$ /CsI molar ratio, and temperature on the oxidative volatilization of iodine from CsI. The optimum conditions were an $FeCl_2$ /CsI molar ratio of 1:1, an oxidation temperature of 500°C, and an oxidation time of 4 h; under these conditions, the iodine removal efficiency was 98.37%. The remaining solids were found to be mainly α - Fe_2O_3 and CsCl, suggesting that $FeCl_2$ was oxidized by air during the reaction while providing Cl⁻ to convert CsI into CsCl, and that iodine was mainly volatilized as I_2 . These results provide experimental support for high-temperature oxidative iodine removal from spent fuel.

1 Introduction

Spent nuclear fuel contains several iodine isotopes. Among them, ^{129}I has a long half-life and high mobility, which makes its capture and subsequent waste treatment difficult during reprocessing. It also tends to accumulate in the thyroid, posing a risk of internal radiation exposure. Therefore, controlling iodine in spent fuel is important for environmental safety and radiation protection. Iodine may exist in various forms during reprocessing, including I^- , I_2 , IO_3^- , organic iodine, and metal iodides; these forms differ noticeably in volatility, reactivity, and capture behavior. In aqueous reprocessing, iodine may also be redistributed among off-gas, aqueous, organic, and subsequent waste streams. Consequently, converting and removing the iodine-containing fractions at the front end, followed by coupling with off-gas purification and subsequent solid-waste treatment, can reduce the difficulty of handling iodine in multiple streams [1–3]. In oxide spent fuel, cesium and iodine can form relatively stable CsI; therefore, CsI can serve as a non-radioactive surrogate compound for studying iodine volatilization and solid-phase conversion [4].

During voloxidation, iodine release depends not only on temperature but also on the oxidation state of the fuel matrix and the gas atmosphere composition. Early studies showed that shearing spent fuel followed by oxidation and pulverization in air or oxygen could promote the release of a portion of volatile fission products before dissolution [5]. Hiernaut et al. [6] further investigated the behavior of volatile fission products during the oxidation of irradiated UO_2 to U_3O_8 , finding that the oxidation state of the fuel matrix affected the release of volatile components. For systems containing CsI and fuel oxides, Sunder [7] used a high-temperature Knudsen-cell mass spectrometer to study the relationship between oxidation state and iodine volatility. It was found that when molybdenum was oxidized to MoO_3 , the I_2^+/CsI^+ signal

ratio increased significantly, which was attributed to the conversion of CsI into elemental iodine. Collins et al. [8] also found that the carrier-gas composition changed the release forms of iodine and cesium: in helium or steam–helium–hydrogen atmospheres iodine release resembled CsI, whereas in dry air it was closer to elemental iodine. Thus, both the oxidation state and reaction atmosphere affect iodine release from CsI.

For stable solid CsI, simply increasing the temperature or oxidation capacity cannot guarantee effective iodine removal. HSC equilibrium simulations that treat the whole fuel system have incorporated Cs–O and Cs–I interactions into high-temperature voloxidation analysis; however, such calculations mainly describe phase equilibria in complex fuel systems and cannot replace direct experimental verification of pure CsI solid-phase conversion [9]. In recent years, NO₂-mediated advanced voloxidation has provided direct evidence for changing the composition of solid CsI. Johnson et al. [10] treated CsI surrogates in a cyclic NO₂/O₂ atmosphere and observed conversion of CsI into CsNO₃, with iodine removal efficiencies of 46%–100%; higher removal efficiencies required multiple replenishments of NO₂, and the results were influenced by surface moisture and NO_x composition. Another approach uses chlorine-containing reactants for halogen substitution. Jeon et al. [11] studied the chlorination reaction kinetics of CsI under cladding hull waste treatment conditions by thermogravimetry, showing that Cl₂ can provide a reaction path for converting CsI into CsCl and releasing iodine-containing volatile products. However, Cl₂ causes equipment corrosion and increases the burden on off-gas purification [3].

The above studies demonstrate that oxidizing atmospheres can influence the chemical form and volatility of iodine, but to achieve significant conversion of stable CsI a component capable of reacting with CsI must be introduced. Existing studies have mainly focused on whole-fuel oxidation [5–8], NO₂-mediated advanced oxidation [10], or gas-phase chlorination [11]. Direct comparisons of pure CsI treated with 7% ozone, oxygen, and air, as well as studies on the combined effect of auxiliary components and oxidizing atmosphere, remain limited. Therefore, it is necessary to examine the effects of oxidizing atmosphere and auxiliary components on CsI iodine removal.

In this study, CsI was treated with 7% ozone, pure O₂, and air, and the iodine removal efficiencies before and after adding FeCl₂ were compared. In the FeCl₂-assisted system, the effects of reaction time, FeCl₂/CsI molar ratio, and reaction temperature were further investigated. Iodine removal efficiency was determined by ion chromatography, and the phase composition, elemental distribution, and surface chemical states of the products were analyzed by X-ray Diffraction, Scanning Electron Microscope-Energy Dispersive Spectrometer, and X-ray Photoelectron Spectroscopy; these results were then used to discuss the possible reaction process.

2 Experimental

2.1 Reagents and materials

CsI (99.9%, Shanghai Macklin Biochemical Co., Ltd.) and anhydrous FeCl₂ (99.7%, Xi'an Tianmao Baoding Bio-Technology Co., Ltd.) were used without further purification. The experimental gases included air, pure O₂, and ozone (7%) generated by a TITAN-30 ozone generator. For ion chromatography calibration, I⁻ standard solutions of 20, 40, 60, 80, and 100 mg L⁻¹ were used, and the eluent was 17 mmol L⁻¹ NaOH solution.

2.2 Experimental apparatus and general procedure

As shown in Fig. 1, the reaction was carried out in a thermogravimetric analyzer with controllable temperature and atmosphere. CsI and FeCl₂ were weighed in the prescribed molar ratio and thoroughly mixed, then placed in a quartz crucible with an outer diameter of 10 mm and a height of 10 mm. After the desired gas was introduced, the system was heated to the target temperature at a heating rate of 20°C min⁻¹ and held at that temperature under a gas flow rate of 1.5 L min⁻¹. After the reaction, the sample was cooled to room temperature, the solid product was collected, and the residual iodine was determined by ion chromatography.

2.3 Determination of residual iodine in the solid and iodine removal efficiency

After the reaction, the solid was dissolved and leached with 100 mL of deionized water, and an excess of ascorbic acid was added to reduce iodine in different oxidation states in the leachate to I⁻. After filtration and 10-fold dilution, I⁻ was determined by ion chromatography. The I⁻ concentration in the leachate was calculated from the chromatographic peak area and the standard curve, and the residual iodine mass in the solid after reaction was then calculated from the leachate volume and dilution factor. The iodine removal efficiency η was calculated according to Eq. (1):

$$\eta = (m_0 - m_r) / m_0 \times 100\% \quad (1)$$

where m_0 is the mass of iodine in the initial CsI, and m_r is the residual iodine mass measured in the solid after reaction. This index represents the extent of iodine removal from the solid after reaction.

2.4 Product characterization

The phases of the solids before and after reaction were analyzed by X-ray diffraction. The particle morphology was observed by scanning electron microscopy. Energy-dispersive X-ray total spectra and Fe, O, and I elemental mappings were acquired at 20 kV to analyze the spatial distribution of the main elements.

XPS measurements were performed on a PHI GENESIS photoelectron spectrometer using monochromatic Al K α radiation (1486.6 eV). Survey spectra and regional spectra of C 1s, O 1s, Fe 2p, Cl 2p, I 3d, and Cs 3d were collected. All binding energies were calibrated globally against the surface adventitious C 1s peak at 284.8 eV. The regional spectra were fitted by constrained nonlinear least

squares using a quadratic polynomial background and Gaussian–Lorentzian mixed peak shapes. Cl 2p, I 3d, and Cs 3d were constrained by spin–orbit splittings of 1.60, 11.40, and 14.00 eV and area ratios of 2:1, 3:2, and 3:2, respectively; the same doublet pair shared a common full width at half maximum. The Fe 2p_{3/2} region was fitted using a Fe(III) multiplet envelope model. In the Cs 3d region, the Fe 2p_{1/2} component overlapping with Cs 3d_{5/2} was explicitly included; therefore, the Fe²⁺/Fe³⁺ ratio was not calculated from this region.

3 Results and discussion

3.1 Determination of the oxidation system

(1) Effect of single oxidizing atmospheres on CsI

Comparative experiments were performed without adding FeCl₂ to determine whether a single oxidizing atmosphere alone can directly promote iodine volatilization from CsI. 7% ozone and pure O₂ were used as the oxidizing atmospheres at 300°C and 400°C. The effect of the single atmosphere on the oxidative volatilization of iodine from CsI was evaluated by comparing the normalized solid-phase mass before and after treatment and by XRD analysis of the products.

The results are shown in Fig. 2. At 300°C and 400°C, the solid-phase masses of the four groups treated with 7% ozone and O₂ were all close to the CsI raw-material baseline of 100%, with a maximum deviation of 0.104%. No obvious weight loss corresponding to iodine volatilization was observed. Representative XRD results are shown in Fig. 3. The treated products were still dominated by characteristic CsI peaks; in the locally enlarged 24°–32° region, weak diffraction signals consistent with CsI₂O₃ were visible only for the 7% ozone-treated product, indicating that only a small amount of CsI was oxidized under the single atmosphere and most iodine remained in the solid phase.

Therefore, in the range of 300–400°C, neither 7% ozone nor O₂ alone caused obvious solid-phase weight loss of CsI, and iodine could not be removed effectively by volatilization. A mere increase in the oxidizing power of the gas was insufficient to break the stable solid structure of CsI; therefore, an auxiliary component capable of reacting with CsI in the solid phase needs to be introduced.

(2) Comparison of FeCl₂-assisted oxidation under different atmospheres

To investigate the effect of FeCl₂ on CsI iodine removal, FeCl₂ was added to the system. At 450°C, experiments were conducted using a FeCl₂/CsI molar ratio of 2:3, a holding time of 3 h, and a gas flow rate of 1.5 L min^{−1}, and the reaction results under different oxidizing atmospheres were compared. As shown in Fig. 4, the average iodine removal efficiencies under 7% ozone, pure O₂, and air were 95.305%, 96.880%, and 97.125%, respectively.

The average iodine removal efficiencies under the three atmospheres were close to each other, indicating that the atmosphere type had little effect on the iodine removal efficiency from Csl and that the O₂ in air was sufficient for the reaction. Considering that air does not require ozone generation or high-purity O₂, all subsequent experiments used air as the reaction atmosphere.

3.2 Optimization of oxidation conditions

(1) Effect of reaction time

The atmosphere comparison results showed the potential of air serving as the reaction atmosphere for the FeCl₂-assisted oxidation system. On this basis, the effects of reaction time, FeCl₂/Csl molar ratio, and reaction temperature on the iodine removal efficiency were then investigated. At 450°C, FeCl₂/Csl molar ratio of 2:3, and air atmosphere, the effect of reaction time on iodine removal efficiency was investigated; the results are shown in Fig. 5. At 0.5, 1, 2, 3, 4, and 6 h, the iodine removal efficiencies were 64.2%, 66.7%, 66.8%, 71.6%, 73.01%, and 72.6%, respectively. The iodine removal efficiency increased overall from 64.2% to about 72.6%, changed little between 3 and 6 h, and differed by only about 0.4% between 4 and 6 h. This trend is consistent with the time-dependent conversion behavior reported for Csl treatment [10, 11]. Therefore, a reaction time of 4 h was selected for the subsequent experiments.

(2) Effect of FeCl₂/Csl molar ratio

To investigate the effect of FeCl₂ dosage on the iodine removal efficiency, the FeCl₂/Csl molar ratio was varied at 450°C under an air atmosphere with a holding time of 4 h. As shown in Fig. 6, as the molar ratio increased from 0.25 to 1.0, the iodine removal efficiency increased gradually, indicating that increasing the FeCl₂ dosage promoted the reaction. At low molar ratios, the FeCl₂ amount and its contact with Csl may be insufficient; with more FeCl₂, more Csl molecules participated in the reaction. This trend is consistent with the role of reagent availability described for Csl chlorination kinetics [11]. When this ratio increased from 1.0 to 1.50, the removal efficiency improved only slightly, with an average removal efficiency of approximately 98.6%. This may be attributed to the excess ferrous chloride promoting particle aggregation or coating the Csl surface, thereby reducing the effective gas–solid contact area. Therefore, a FeCl₂/Csl molar ratio of 1:1 was selected for subsequent experiments.

(3) Effect of reaction temperature

Subsequently, the effect of reaction temperature was investigated at an FeCl₂/Csl molar ratio of 1:1, holding time of 4 h, and air atmosphere; the results are shown in Fig. 7. The experimental temperatures ranged from 300°C to 600°C. From 300°C to 500°C, the iodine removal efficiency increased overall. The average iodine removal efficiencies at 450°C and 500°C were 96.85% and 98.37%, respectively, indicating that raising the temperature to 500°C still favored the Csl reaction. This temperature dependence agrees with earlier voloxidation studies showing that temperature, fuel-matrix oxidation state, and gas composition jointly affect the release of volatile iodine species [5–8].

Increasing the temperature favored solid-phase contact and reaction and also promoted the oxidation of Fe(II) to Fe(III). However, the average iodine removal efficiencies at 500, 550, and 600°C were 98.37%, 97.85%, and 98.17%, respectively. These values remained relatively high. Further increasing the temperature did not improve the average iodine removal efficiency and would only increase energy consumption. Therefore, 500°C was considered a relatively suitable reaction temperature.

3.3 Analysis of oxidation products

(1) Phase analysis

XRD analysis was performed on the residue obtained at 500°C under an air atmosphere with an FeCl₂/CsI molar ratio of 1:1 and a holding time of 4 h to identify the phases formed after the reaction and to assess the phase change of CsI after iodine volatilization. As shown in Fig. 8, α -Fe₂O₃ and CsCl were detected in the residue. The formation of α -Fe₂O₃ indicates that Fe(II) in FeCl₂ was oxidized to Fe(III) oxide by air; the formation of CsCl indicates that Cs⁺ in CsI was converted into chloride. Compared with the results where CsI remained dominant after treatment with either 7% ozone or O₂ alone (as shown in Fig. 3), the appearance of α -Fe₂O₃ and CsCl shows that FeCl₂ participated in the reaction and the original CsI structure changed.

In addition, α -Fe₂O₃ is weakly magnetic; therefore, the iron-containing product after reaction could potentially be separated magnetically, providing a possible route for iron removal and recovery.

(2) SEM-EDS morphology and elemental distribution

To characterize the particle morphology of the reaction product at different scales and the distribution of iron, oxygen, and residual iodine, SEM-EDS analysis of the product was performed at 20 kV. The 5000× image in Fig. 9(a) shows that the product mainly consisted of irregular micrometer-sized agglomerates, with a large number of fine particles attached on the surface of larger agglomerates. The 50000× image in Fig. 9(b) further shows that local particles were composed of stacked submicrometer flakes or polyhedral grains, accompanied by even finer attached particles.

Characteristic signals of Fe, O, and I could be distinguished in the EDS total spectrum. The elemental mapping results showed that Fe and O covered the main particle regions, and their distribution corresponded to the α -Fe₂O₃ detected by XRD, indicating that iron oxide was an important component of the reaction product. The I signal was relatively dispersed in the mapped area, indicating that a small amount of residual iodine remained on the solid surface after reaction; combined with the high iodine removal efficiency measured by ion chromatography, most iodine had been removed.

(3) XPS analysis of surface chemical states

To analyze the chemical states of the main elements on the surface of the reaction product, XPS analysis was performed. The elemental composition was examined using the survey spectrum, and the

high-resolution Cs 3d, I 3d, O 1s, and Cl 2p spectra were energy-calibrated and peak-fitted. As shown in Fig. 10, signals of C, O, Fe, Cl, I, and Cs were observed in the survey spectrum, and the fitted curves agreed well with the raw data in each high-resolution region.

The O 1s spectrum could be divided into two components at approximately 528.84 and 531.59 eV, which were assigned to lattice oxygen and surface-adsorbed or hydroxyl-related oxygen species, respectively. The Cs 3d and Cl 2p spectra showed the corresponding spin-orbit doublets, indicating the presence of Cs- and Cl-containing species on the product surface. Because the differences in core-level binding energies among different cesium salts are small, the identification of CsCl was mainly based on the XRD results.

The fitted peak positions of the I 3d_{5/2} and I 3d_{3/2} doublets were approximately 621.81 and 633.21 eV, respectively, with a spin-orbit splitting of 11.40 eV, indicating that a small amount of residual iodine remained on the product surface. The XPS results confirmed the presence of Cs, Cl, Fe, O, and residual I on the product surface, consistent with the XRD and SEM–EDS results.

3.4 Analysis of the reaction process

The single-atmosphere experiments showed that although O₂ and 7% ozone could oxidize CsI to some extent, they could not provide effective iodine volatilization. After adding FeCl₂, the iodine removal efficiency increased significantly. Thus, the iodine removal performance depended not only on the gaseous oxidant but also on the solid-phase reaction involving FeCl₂.

α-Fe₂O₃ and CsCl were detected in the solid after reaction, indicating that Fe in FeCl₂ was oxidized by air while Cs in CsI was converted into CsCl. SEM–EDS and XPS detected Fe, O, Cs, Cl, and a small amount of residual I. It can therefore be concluded that FeCl₂ acted both as the precursor of the iron oxide and as the source of Cl[−] for CsCl formation.

From the initial elemental composition of the system, the possible iodine-containing products mainly include I₂, HI, HIO₃, CsIO₃, CsIO₄, and Fe(IO₃)₃ or Fe(IO₄)₃. As shown in Table 1, the formation of HI and HIO₃ both require a hydrogen source. Although air contains a small amount of water vapor, anhydrous FeCl₂ was used in this study and no hydrogen-containing substance was additionally introduced; therefore, the hydrogen source in the system was insufficient, which was unfavorable for the formation of large amounts of HI and HIO₃. In addition, iodine in HI is still in the −1 oxidation state, which is inconsistent with the oxidation direction of I[−] in an oxidizing atmosphere; even if a small amount of HI formed, it would be readily further oxidized. The formation of HIO₃ requires further oxidation of I[−] from −1 to +5, and HIO₃ is difficult to remain stable at the high temperatures used in this study; therefore, HIO₃ cannot be a major iodine-containing product. If CsIO₃, CsIO₄, and iron iodates or periodates were formed in large amounts, their crystalline phases would remain in the solid after the reaction. However, the XRD pattern of the product mainly showed α-Fe₂O₃ and CsCl, and no characteristic diffraction peaks

attributable to the above iodine-containing solid phases were observed, indicating that these species were not formed in detectable amounts and could be excluded as major products. I₂ formed by the oxidation of I⁻ readily enters the gas phase at the experimental temperatures, which is consistent with the formation of CsCl and α-Fe₂O₃ and the significant decrease in solid-phase iodine content. Therefore, the volatilized iodine was present mainly as I₂.

Table 1
Possible iodine-containing species and their properties

Possible species	Iodine oxidation state	High-temperature stability	Volatility, boiling point, or decomposition behavior
I ₂	0	Can exist as a gas-phase molecule under the experimental temperatures	Normal boiling point ~ 184.3°C; easily enters the gas phase at 400–500°C [15]
HI	–1	Unfavorable for stable formation in a dry oxidizing atmosphere	Normal boiling point ~ – 35.4°C, but formation requires a hydrogen source [15]
HIO ₃	+ 5	Dehydrates and decomposes on heating; cannot be stable at 400–500°C	Mainly decomposes on heating rather than boiling stably
CsIO ₃	+ 5	Low-volatility solid oxy-salt	Remains in the solid phase or continues to decompose on heating; does not volatilize directly under these conditions
CsIO ₄	+ 7	Decomposes to CsIO ₃ at about 300–350°C [14]	Decomposes on heating; no normal boiling point applicable under these conditions
Fe(IO ₃) ₃ , Fe(IO ₄) ₃	+ 5, +7	If formed, low-volatility solid salts	Usually decompose before boiling; cannot be the main volatile species

Furthermore, Sunder, Collins, Gouello, and Obada et al. [7, 8, 12, 13] also observed the formation of volatile I₂ from CsI in different oxidation systems, further supporting the above conclusion.

According to the above analysis, the overall reaction can be idealized as:



4 Conclusions

Using CsI as a surrogate for spent fuel, this study compared iodine removal by treatment with 7% ozone and pure O₂ alone with FeCl₂-assisted treatment. After treatment with 7% ozone or O₂ alone, the products were still dominated by CsI, with a small amount of cesium iodate-related diffraction peaks,

indicating that although a single oxidizing atmosphere could oxidize CsI to some extent, it could not cause effective iodine volatilization.

After adding FeCl₂, the average iodine removal efficiencies of the CsI system under 7% ozone, pure O₂, and air at 450°C were 95.305%, 96.880%, and 97.125%, respectively. The result for air at 450°C was close to that for the enhanced oxidizing atmospheres.

The residue consisted mainly of α-Fe₂O₃ and CsCl, with a small amount of residual iodine. These phases indicate oxidation of FeCl₂ and conversion of CsI to CsCl, while the solid-phase evidence and physicochemical comparison support I₂ as the main volatile iodine species. The weak magnetism of α-Fe₂O₃ may facilitate separation of the iron-containing residue. Thus, the method achieves high iodine removal using air without continuous ozone or high-purity O₂ supply, while retaining Cs as CsCl.

Declarations

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Author Contribution

M completed the experimental work and the drafting of the main text; J and H provided assistance with data processing and writing guidance. All authors have reviewed the paper.

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Data Availability

The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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Figures

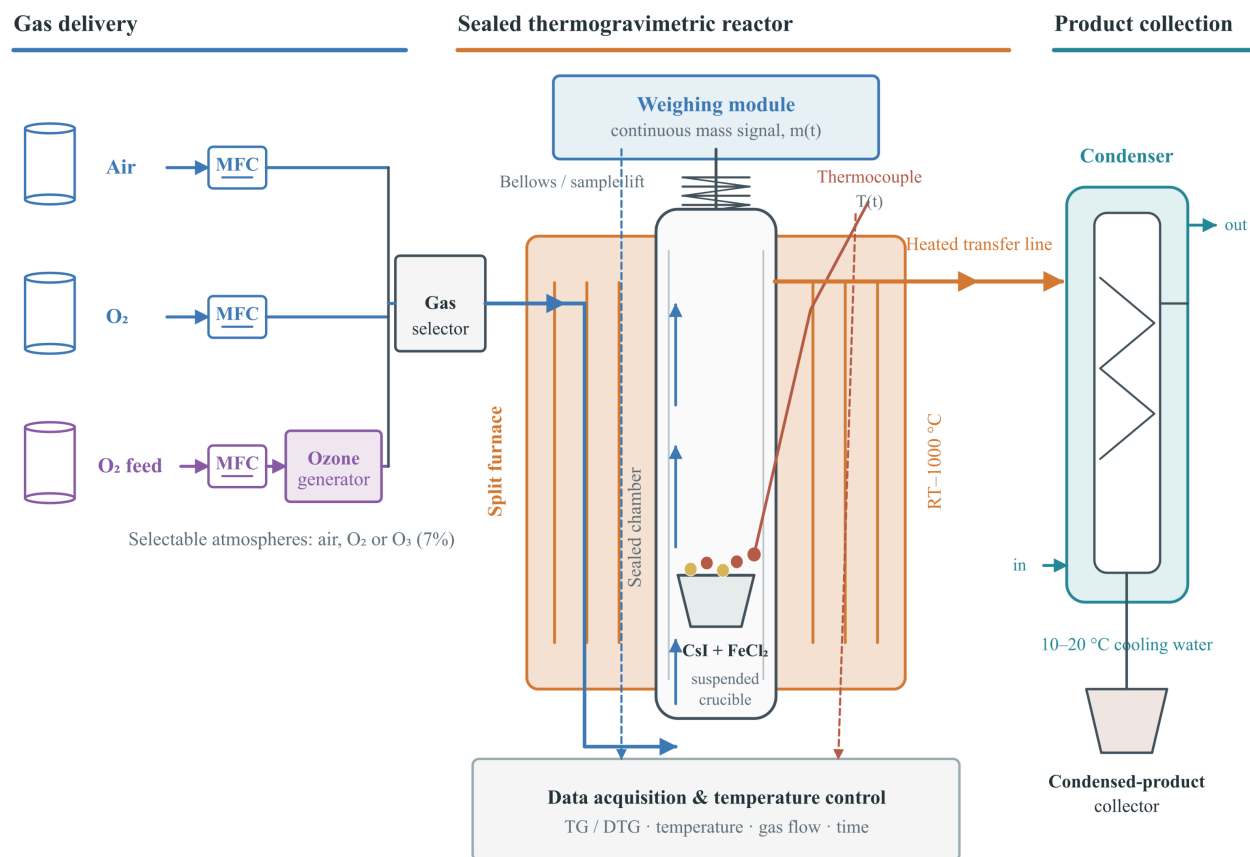


Figure 1

Schematic diagram of the reaction apparatus.

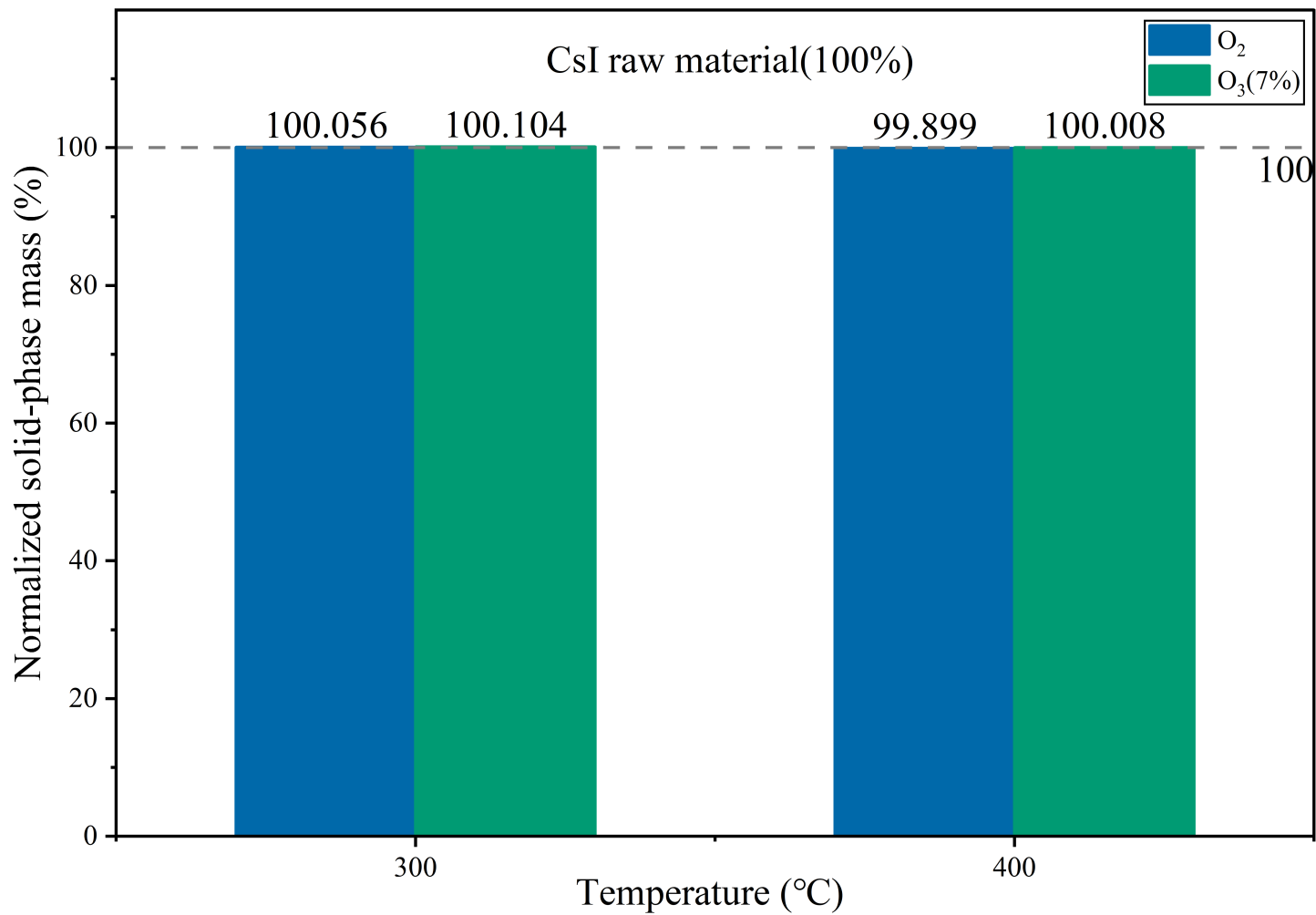


Figure 2

Comparison of solid-phase mass after treatment of CsI with 7% ozone and O_2 at 300 °C and 400 °C.

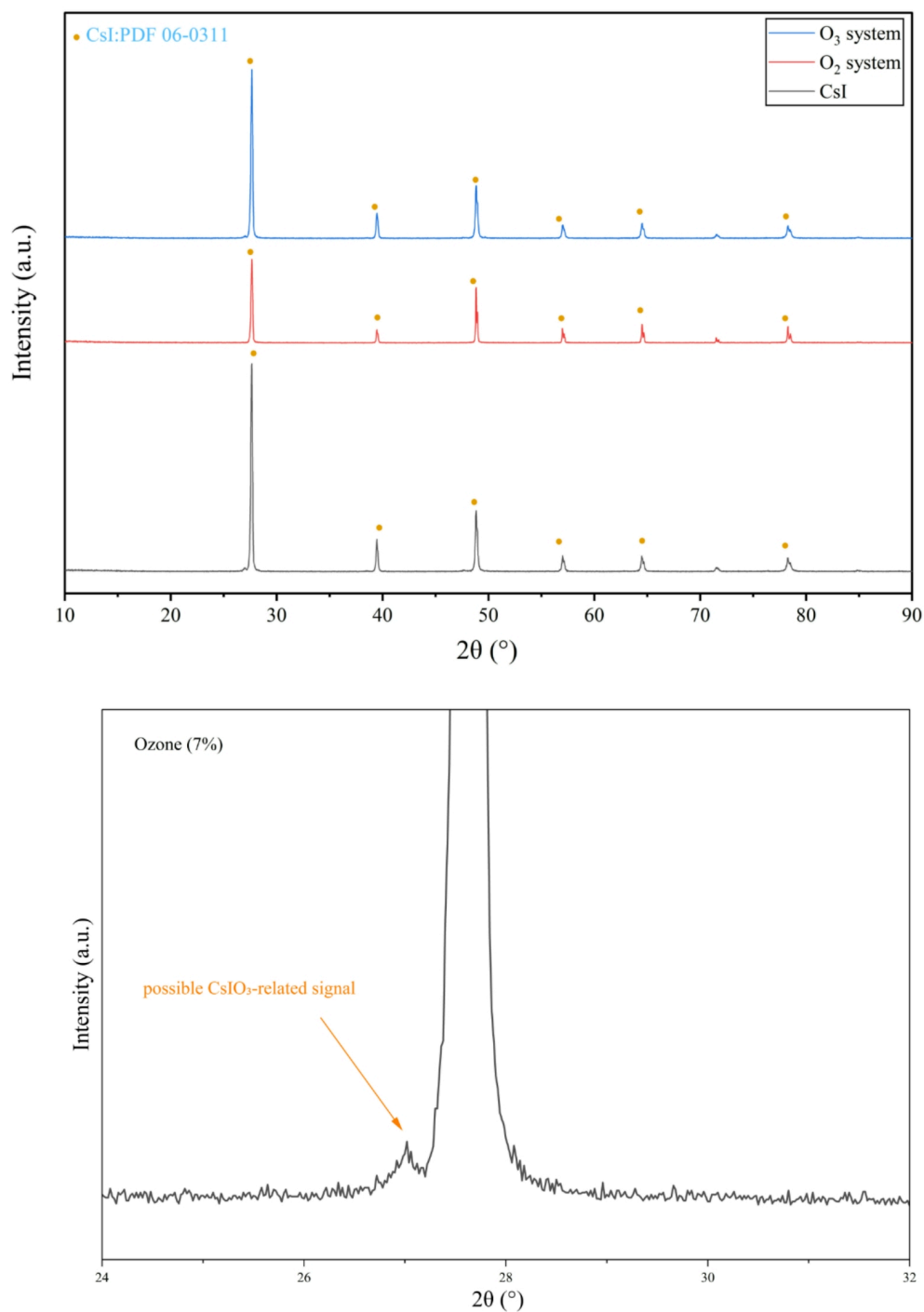


Figure 3

XRD results before and after treatment under single oxidizing atmospheres: (a) XRD patterns of CsI raw material, products treated with pure O₂ and 7% ozone at 400 °C (orange dots mark CsI peaks, PDF 06-0311); (b) locally enlarged 24°–32° region for the 7% ozone-treated product showing weak diffraction signals consistent with CsIO₃.

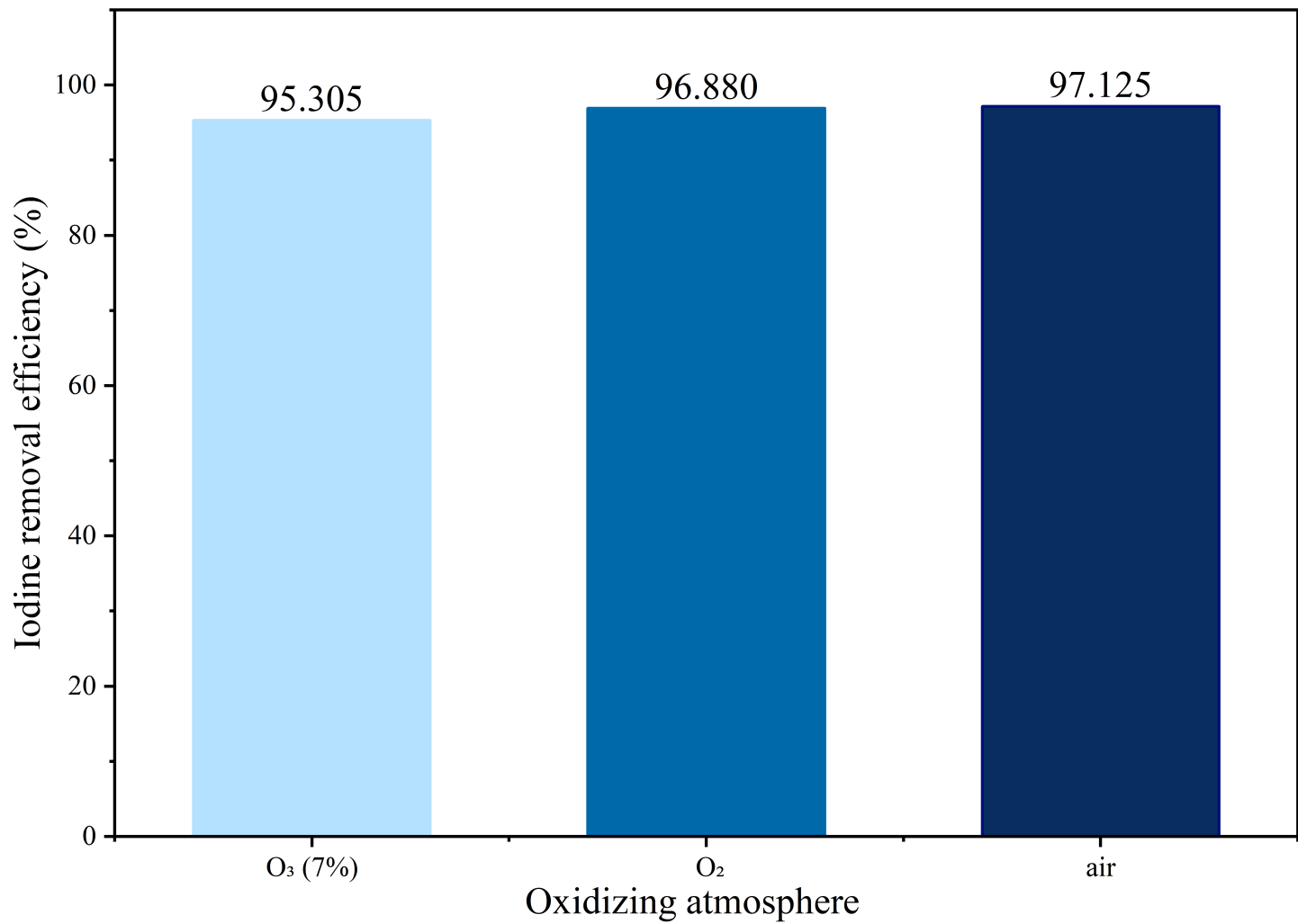


Figure 4

Iodine removal efficiency under 7% ozone, pure O₂, and air at 450 °C, respectively.

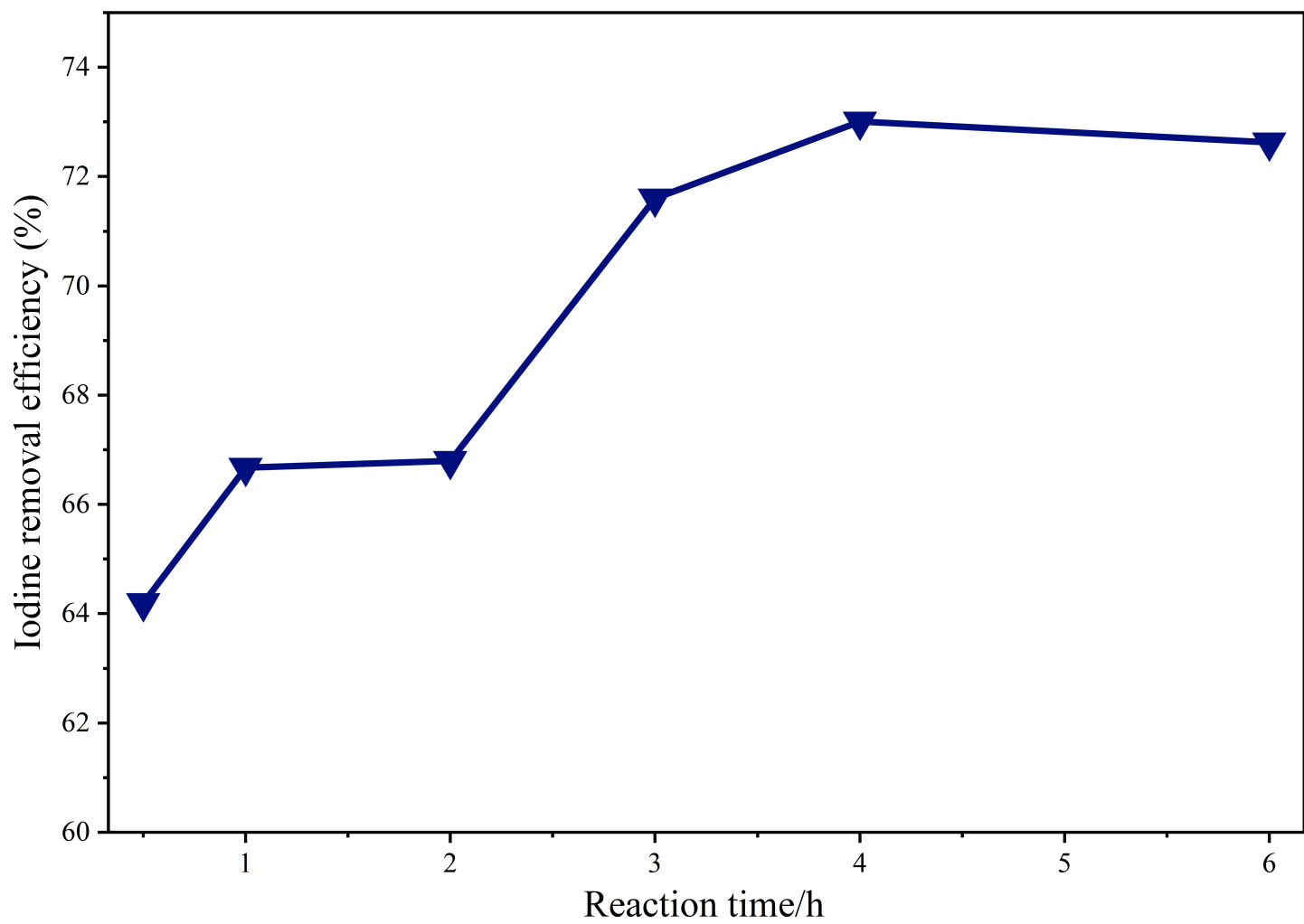


Figure 5

Variation of iodine removal efficiency with reaction time under air.

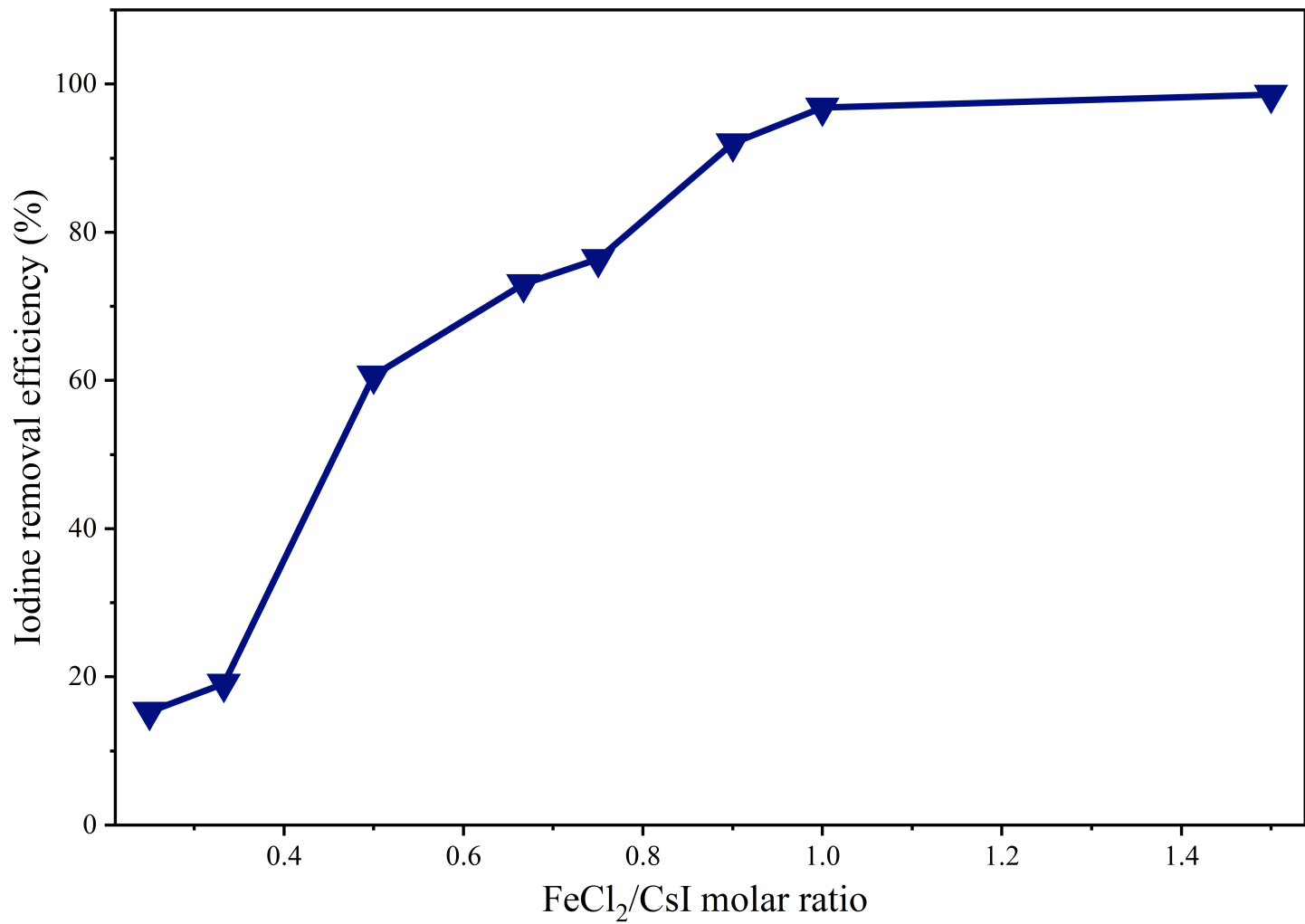


Figure 6

Variation of iodine removal efficiency with FeCl_2/CsI molar ratio in air at 450 °C.

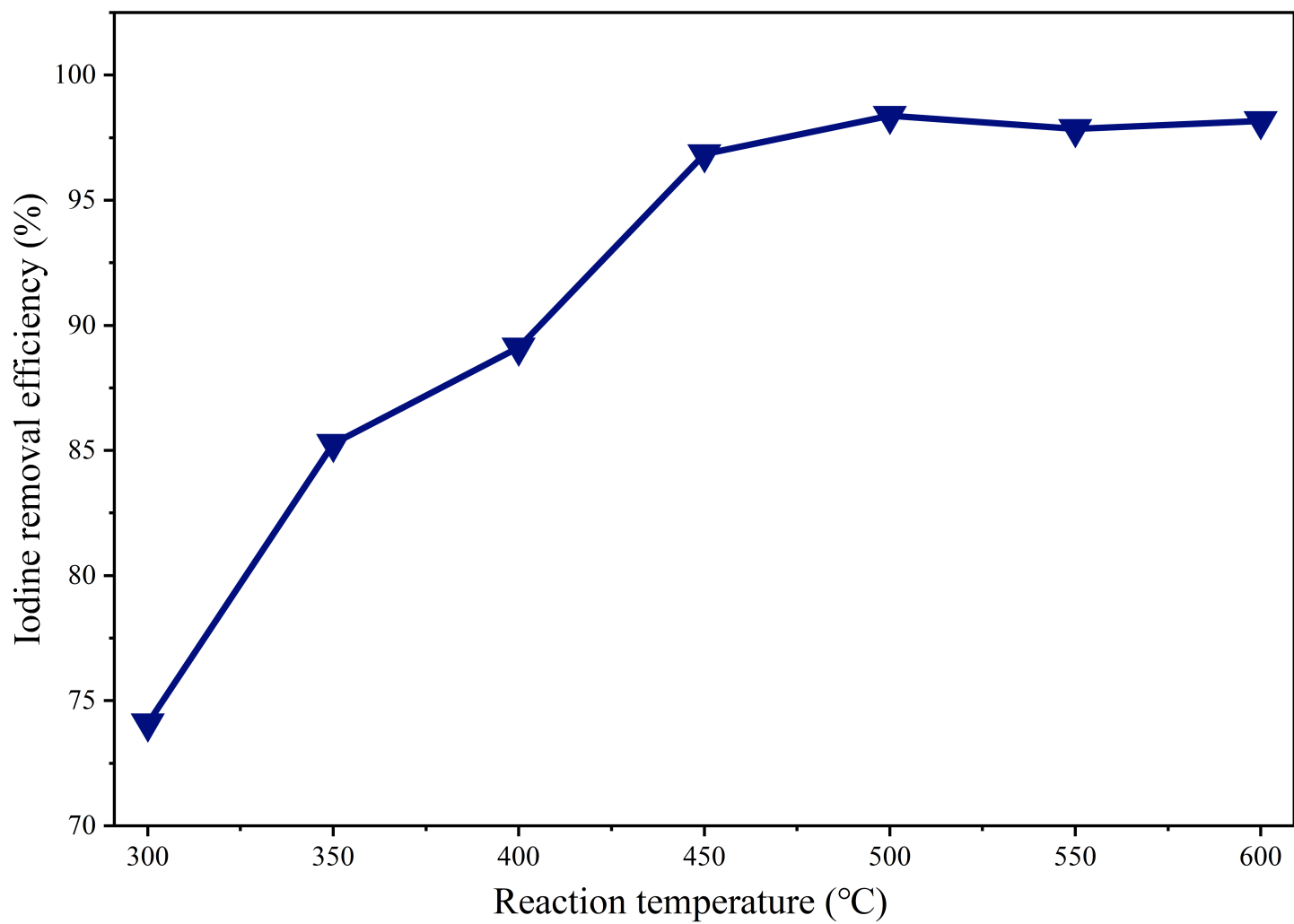


Figure 7

Variation of iodine removal efficiency with reaction temperature under air.

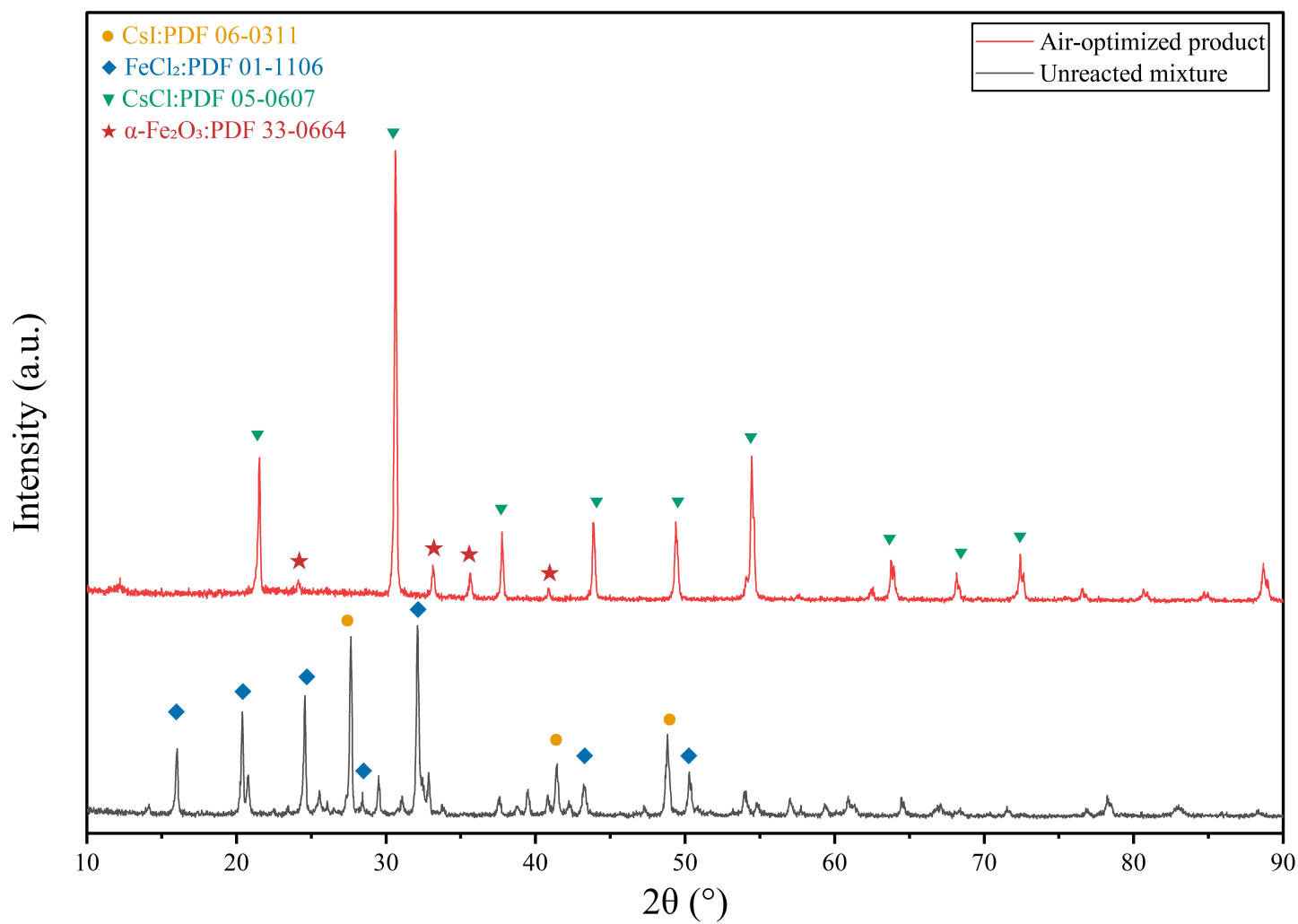


Figure 8

XRD patterns of the unreacted mixture and the product obtained under optimized air conditions.

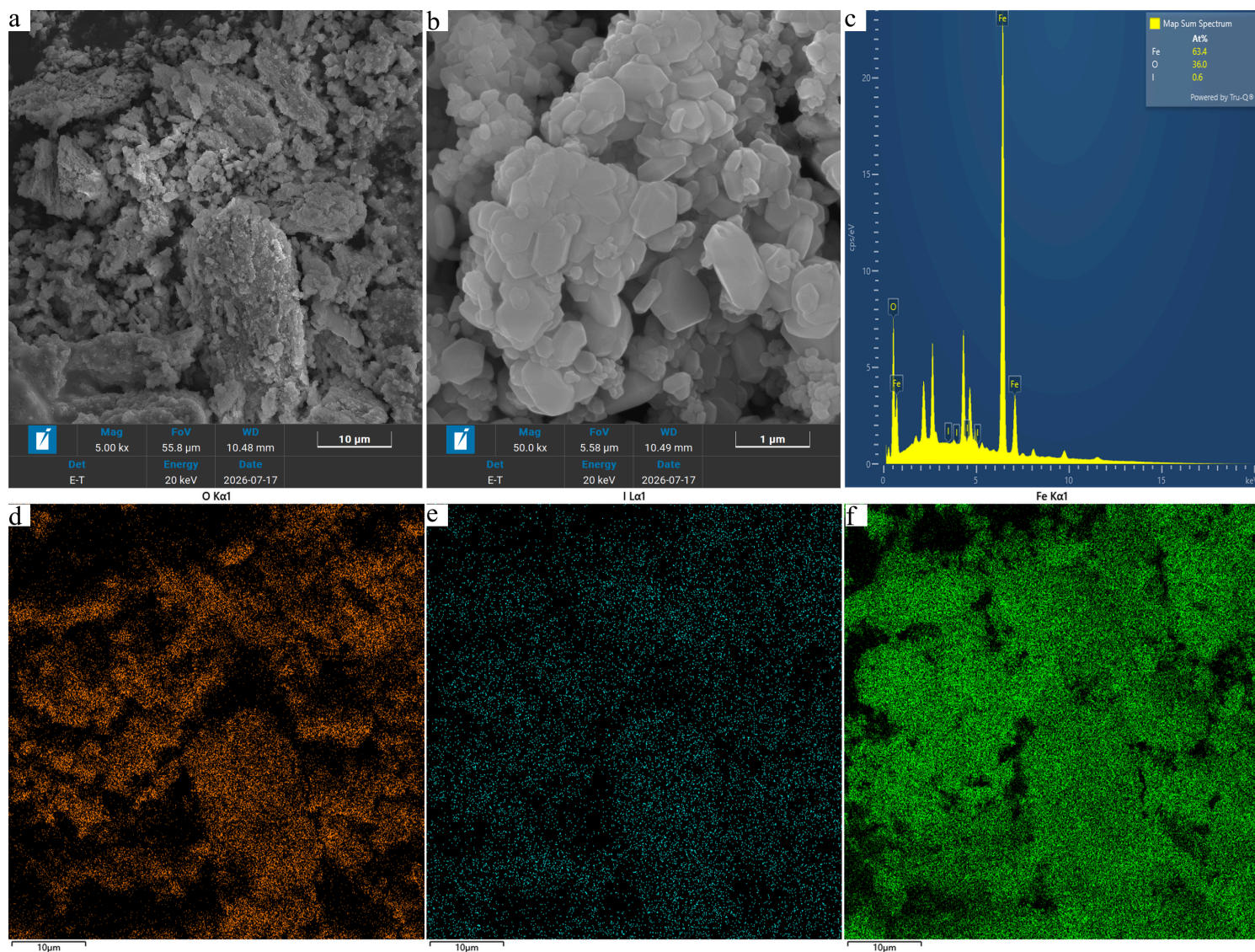


Figure 9

SEM morphology and EDS results of the reaction product: (a) 5000 $\times$ SEM image; (b) 50000 $\times$ SEM image; (c) total spectrum of the mapped region; (d–f) elemental mappings of O, I and Fe.

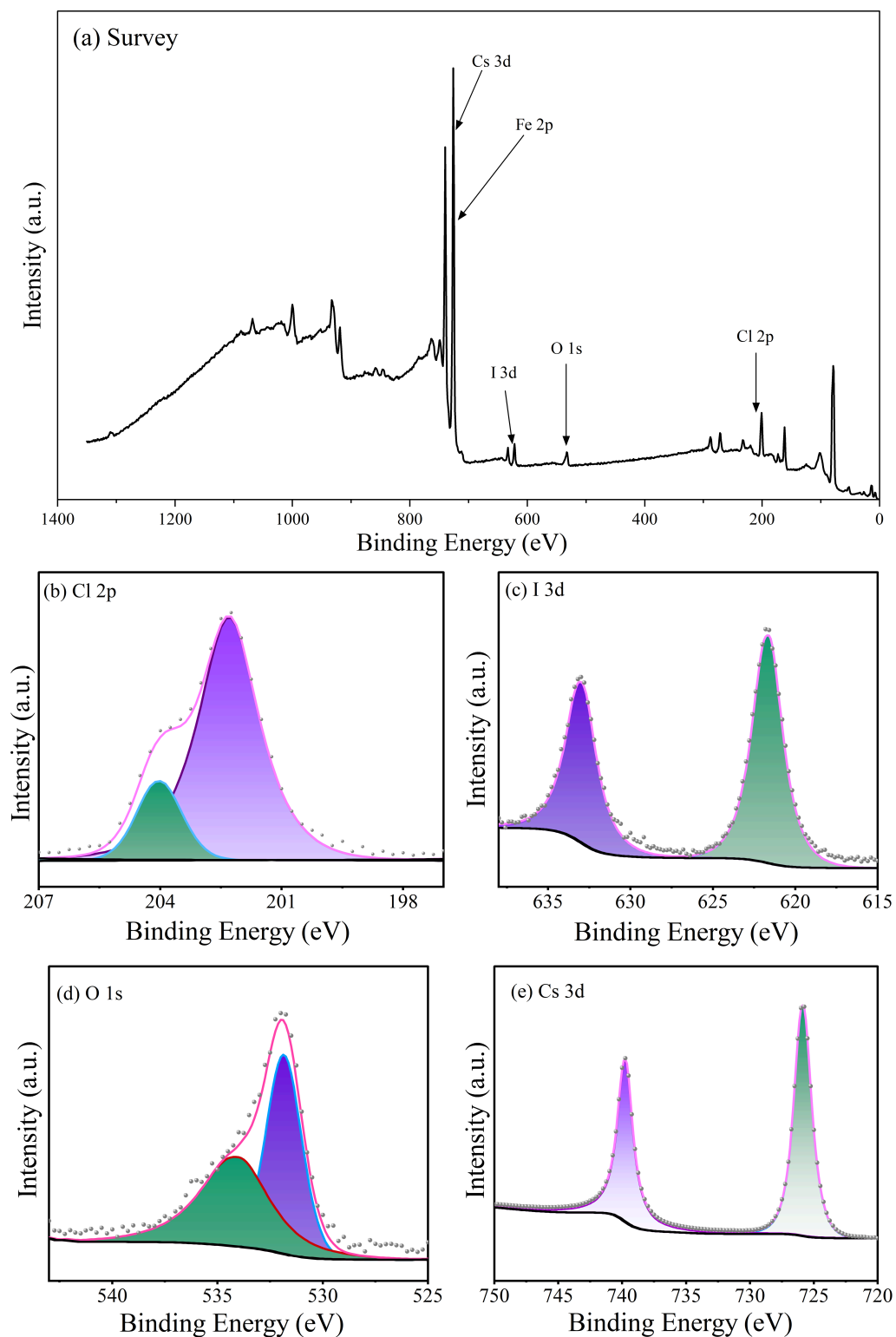


Figure 10

XPS survey spectrum, high-resolution spectra, and peak-fitting results of the reaction product: (a) survey spectrum; (b) Cl 2p; (c) I 3d; (d) O 1s; (e) Cs 3d.