Evolution of Mercury from Iron Ores in Temperature-Programmed Heat Treatments

Javzandolgor BUD, Yuuki MOCHIZUKI and Naoto TSUBOUCHI*

Center for Advanced Research of Energy and Materials, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, 060-8628 Japan.

(Received on June 30, 2021; accepted on September 17, 2021)

The behavior of Hg released from iron ores during temperature-programmed heat treatments (TPHTs) in air has been mainly studied using an online monitoring method. The Hg release behavior in TPHT significantly depends on the type of ore being processed, which includes forms evolved as Hg^0 and Hg^{2+} , and forms that remain thermally stable up to 950°C. In addition, the TPHT experiments for model Hg compounds suggested the presence of several types of Hg forms (HgCl_2 , Hg_2Cl_2 , HgS , HgO , HgSO_4 , and associated mineral-Hg) in the iron ores used. The amounts and proportions of suggested forms of Hg species substantially depend on the type and composition of the iron ore used. These observations may be important in designing an efficient method for the removal of Hg from iron ore and gaseous Hg.

KEY WORDS: iron ore; temperature-programmed heat treatment; mercury; evolution; ironmaking.

1. Introduction

Mercury is one of the most hazardous elements, and it spreads into the environment from many sources. The total amount of mercury emitted in nature was $2\,500 \pm 500$ t/year in 2018,¹⁾ and the mercury emitted in the environment does not disappear or fade away, instead, it changes its form, and exists in nature for decades. Mercury emissions are not only a local problem anymore; they spread across the world through the air, water, and even via the food chain, and adversely affect human health.²⁾ Following the accelerated development of population and consumption, the manufacturing industry continues to grow annually; however, mercury emissions have become more dangerous in several sectors.³⁾ Most of the Hg emissions originate from Asia; in particular, East and Southeast Asia produce 39% of the total global emissions, and industrial fields and fossil fuel usage are the primary sources of Hg emissions in this region. Ferrous and non-ferrous metal productions are primary anthropogenic sources worldwide.⁴⁾ In the field of energy production, coal combustion has the highest percentage of mercury emission sources. Consequently, the control and reduction of emissions are one of the primary challenges facing the industry in this century. A number of scientists are working on the determination and measurement of mercury contents in coal and reported sufficient data to elucidate the emission process of Hg from coal combustion and pyrolysis.^{5–11)} Unfortunately, the information and

results available on the existence and evolution behavior of Hg from iron ore, which is a major raw material for the metallurgic industry and pig-iron and steel productions, are insufficient. However, the availability of data and information on the release forms and behavior of Hg will facilitate the improvement of the emission control and reduction technology. Recently, various Hg removal processes have been adopted, such as coal washing, air pollution control devices (APCDs), and wet flue gas desulfurization (FGD).¹²⁾ However, improving the removal methods and elucidating the release behavior of Hg from iron ore, as well as mercury adsorption from steel production and iron ore applications, remains crucial. To define the existence of Hg species in iron ores and determine their release behavior from iron ore, this study was conducted to examine the interaction between Hg species and other substrates.

2. Experimental

2.1. Iron Ore Sample

One Australian limonite (AUL) and four types of hematite (INH, AUH, BRH, and ISH) mined from different countries (India, Australia, Brazil, and South Africa) were used in this study. These particle sizes were $-250\ \mu\text{m}$. All samples were obtained from the Japan Iron and Steel Federation. **Table 1** presents the compositions of all iron ores used. The total Fe and Hg contents of the samples ranged from 57–67 mass%-dry and 79 to 305 dry $\mu\text{g/g}$, respectively. The gangue components and combined-water (H_2O) contents in the samples (all in mass%-dry) were as follows:

* Corresponding author: E-mail: tsubon@eng.hokudai.ac.jp

Table 1. Gangue components of iron ore samples used in this study.

Sample	Country	Code	Composition, mass%-dry											Hg $\mu\text{g/g}$
			Total-Fe	Si	Al	Fe(II)	Mn	P	Ti	Ca	Mg	S	H ₂ O	
Limonite	Australia	AUL	57.1	2.3	1.2	–	0.09	0.04	0.07	0.16	0.11	0.01	9.16	101
Hematite	India	INH	61.8	2.0	1.1	1.0	0.70	0.06	0.05	0.01	0.03	0.01	4.1	82
Hematite	Australia	AUH	62.8	1.6	0.96	0.15	0.13	0.08	0.04	0.02	0.03	0.02	4.4	227
Hematite	Brazilia	BRH	66.2	0.55	0.57	–	0.60	0.05	0.04	0.01	0.02	0.01	1.72	305
Hematite	South Africa	ISH	66.9	1.2	0.5	0.3	0.02	0.05	0.02	0.05	0.01	0.01	0.37	79

Si, 0.55–2.3; Al, 0.5–1.2; Mn, 0.02–0.7; P, 0.04–0.08; Ti, 0.02–0.07; Ca, 0.01–0.16; Mg, 0.01–0.11; S, 0.01–0.02; and H₂O, 0.37–9.16 mass%.

2.2. Temperature-Programmed Heat Treatment (TPHT)

The TPHT experimental was carried out by flow-type quartz made fixed-bed reactors. The apparatus was shown in Fig. S1 in Supporting Information. First, 5.0-g iron ore sample was charged in a quartz cell and placed into the reactor, and then the reactor was heated up to 950°C by a 10°C/min rate in air flow. The temperature of the K-type thermocouple reactor was maintained. The details of this apparatus have been described in.¹²⁾

2.3. TPHT for Hg Pure Compounds and Mixtures of Hg Compounds and Fe₂O₃

The TPHT operations of several model Hg compounds were also conducted to investigate the nature of Hg release from iron ore. As experimental samples, we prepared physical mixtures of iron oxide (99.9%) with various commercially available Hg species (HgCl (99%), HgCl₂ (99.5%), HgS (99%), HgO (98%), and HgSO₄ (99%)) in proportions selected to ensure a mercury concentration of 100 mg/g for each mixture. Particle size of all reagents used were $\sim 250 \mu\text{m}$. It should be noted that the mercury content should originally be 100 $\mu\text{g/g}$ to match the mercury concentration in the ore; however, the amount was significantly small that it was difficult to measure it by weight during the preparation of Fe₂O₃/Hg compound mixtures. The general term “Hg compound/Fe₂O₃” is used to refer to these mixtures. Mixture samples were subjected to TPHT via the procedure described above for iron ore, and total Hg was solely analyzed. In this study, the reproducibility and analytical errors were within $\pm 10\%$ and $\pm 5\%$, respectively, for measurements of gaseous Hg and Hg in the solid phase.

2.4. Hg Analysis

Hg was measured in the as-received iron ore and solid sample after the TPHT was conducted via mixed acid dissolution¹²⁾ and reduction using cold vapor atomic absorption spectrometry (AAS) (Hiranuma Sangyo, HG-450). Gaseous total-Hg, which evolved in TPHT, was analyzed at 1-s intervals by non-dispersive double-beam direct UV AAS using a mercury analyzer (Nihon Instruments, EMP(WLE)-2/SGM-8) equipment and SnCl₂ solution, while Hg⁰ was measured using a KCl solution instead of a SnCl₂ solution. The apparatus was shown in Fig. S1 in Supporting Information. The amount of Hg²⁺ was calculated as the difference between

the amount of total Hg released to the released amount of Hg⁰. The release amount of total Hg, Hg⁰, and Hg²⁺ was calculated based on the respective amounts of their content in iron ores. Hg in the ore represents the Hg concentration in the as-received iron ore.

3. Results and Discussion

3.1. Release Behavior of Total-Hg during TPHT of Iron Ore

Figure 1 illustrates the release behavior of total Hg from iron ore samples during TPHT up to 950°C in an air environment. Hg release started at approximately 100°C for all samples; however, release profiles were entirely different for each sample used. For BRH (Fig. 1(a)), the Hg release profile exhibited main and shoulder peaks at 600°C and 800°C, respectively. The Hg evolution was determined up to 950°C. Hg release from AUH (Fig. 1(b)) exhibited broad peaks at 150°C and 550°C, and a distinct major peak was observed at 750–800°C. Figure 1(c) illustrates the Hg release profile of the INH. Hg release was observed at 200°C, and broad main peaks were measured at approximately 600°C. In the case of ISH (Fig. 1(d)), three broad peaks were observed at approximately 200°C, 500°C, and 700°C, respectively. For AUL (Fig. 1(e)), Hg was released above 100°C, and the release profile exhibited shoulder and main peaks at approximately 300°C and 350°C, respectively. Almost no Hg release was observed above 500°C. From these results, it was determined that the total Hg release profile depends on the iron ore type. In other words, the evolution profiles indicate that Hg species in ores may exist in at least four forms (*i.e.*, volatile forms below 400°C, at 400–600 or 700°C, at 600–950°C, and at thermally stable temperatures up to 950°C).

Figure 2 presents the mass balance of the TPHT examination. It was obtained by integrating the formation rate profiles for gaseous total Hg shown in Fig. 1. Gaseous-Hg and solid-Hg in residues ranged from 16% to 73% and 30% to 75%, respectively. The mass balances were within a logical range of $100 \pm 10\%$. The order of solid-Hg was $\text{INH} \approx \text{BRH} < \text{AUH} < \text{ISH} \ll \text{AUL}$. It is observed that Hg in AUL exists in a form that is difficult to release. In contrast, almost 60%–70% of total Hg was released from all ore samples with ease, except for AUL. This may indicate that Hg exists in ores and the release-form because gaseous-Hg are relatively different. In accordance with previous studies,^{5–11)} most of the Hg content in coal evolves in the gaseous form at low temperatures during pyrolysis or combustion. In contrast, 30%–75% of the total Hg content of iron ore remain

Fig. 1. Release behavior of total Hg during TPHT. (a) BRH, (b) AUH, (c) INH, (d) ISH, and (e) AUL. (Online version in color.)

Fig. 2. Distribution of Hg contents for iron ore samples. (Online version in color.)

Fig. 3. Relationship between Hg content in as-received iron ore and released amount of total-Hg. (Online version in color.)

in the solid phase even after heating to 950°C. These results suggest that the Hg content assume significantly different forms in iron ore and coal, which indicates that several thermally stable forms of Hg exist.

Figure 3 presents the results of the relationship between the Hg content in the ores presented in Table 1 and the amount of gaseous Hg in Fig. 2. Although there were a few variations for low Hg-content ores, there was a positive correlation between the Hg content in the ores and the amount of gaseous Hg.

In other words, the ore with higher Hg content has more volatile Hg species, thus suggesting that the Hg content in the ore depends primarily on the thermally unstable mercury species. These results may also guide the development of methods to manage the Hg released during the thermal treatment of iron ore during the steelmaking process.

3.2. Evolution Behavior of Hg^0 and Hg^{2+} during TPHT

The evolution profile of gaseous Hg^0 during TPHT was investigated to elucidate the Hg forms in iron ore. The evo-

Fig. 4. Release profiles of Hg^0 during TPHT. (a) BRH, (b) AUH, (c) INH, (d) ISH, and (e) AUL. (Online version in color.)

Fig. 5. Release profiles of Hg^0 and Hg^{2+} forms during TPHT of iron ore. (a) BRH, (b) AUH, (c) INH, (d) ISH and (e) AUL. (Online version in color.)

lution profiles of Hg^0 from the ore samples are presented in **Fig. 4**. For the BRH sample (**Fig. 4(a)**), the Hg^0 evolution profile exhibited a large and high-intensity peak at 610°C. **Figure 4(b)** presents the Hg^0 profiles of the AUH samples. Release started at 100°C, and provided three smaller peaks than BRH at 150°C, 600°C, and 750°C. Hg^0 evolution from INH (**Fig. 4(c)**) was observed at 200°C, and the profile exhibited two small peaks at 550°C and 650°C, and the Hg^0 release continued until 950°C. In the case of ISH (**Fig. 4(d)**), the Hg^0 evolution profile exhibited two broad peaks at 200°C and 450°C, and a shoulder peak at 700°C. The evolution reached to 950°C. In the case of AUL (**Fig. 4(e)**), almost no Hg^0 evolution was observed. From these results, the Hg^0 evolution also depends on the iron ore type.

Figure 5 summarizes the evolution profiles of the total Hg, Hg^0 , and Hg^{2+} . Here, the Hg^{2+} profiles were determined by calculating the difference between the total Hg and Hg^0 evolution profiles. For BRH (**Fig. 5(a)**), the shoulder peak that was released at 500–550°C in the total Hg profile disappeared in the Hg^0 profile, and the intensity of the main peak at 600°C was similar to the total Hg peak. Nevertheless, the intensity of detachment that appeared at 600–950°C was decreased. Compared with the total Hg, the elimination amount of Hg^0 decreased, which can be attributed to the increased Hg^{2+} elimination. In other words, in the high-temperature range, the total Hg content for the BRH release was in both Hg^0 and Hg^{2+} forms. In **Fig. 5(b)**, the release profile of total-Hg from AUH matched with Hg^0 at 100–250°C and 550–700°C temperature ranges, while the Hg^{2+} profile matched total-Hg at 250–550°C. Compared with the other sample profiles, AUH had the highest Hg^{2+} peak (at approximately 750°C). In the case of INH (**Fig. 5(c)**), the total Hg profile was observed to be similar to that of Hg^0 and Hg^{2+} . Regarding the ISH (**Fig. 5(d)**), total-Hg and Hg^0 nearly matched with each other, and Hg^{2+} release started above 850°C. This shows that there is almost no release of Hg^{2+} from ISH up to 850°C. For AUL (**Fig. 5(e)**), the main peak of the total-Hg appeared at a temperature range of 300–400°C, and at that temperature range, Hg^{2+} also exhibited the main peak. These two peaks had approximately the same formation rate and exhibited a total Hg profile primarily originating from Hg^{2+} . From these results, we can observe that the evolution behavior of Hg^{2+} similarly depends on the iron ore type.

Figure 6 presents the distribution of Hg forms during

TPHT for all five samples used in this study. The AUL sample has the highest percentage of solid-Hg and the lowest Hg^{2+} , while AUH exhibits the highest Hg^{2+} content. The distribution percentages of Hg^{2+} increased in the following order: AUL < ISH < INH < BRH < AUH. When comparing INH, AUH, BRH, and ISH, the ores with higher Hg volatilization rates tend to emit mercury as Hg^0 .

Figure 7(a) presents the relationship between the amount of volatilized total Hg and Hg concentration in iron ore. There was a relatively optimal correlation between the amount of volatilized total Hg and Hg concentration. This correlation was also observed in the case of volatility based on percentage; however, the correlation coefficients were smaller than those in the case of volatility based on weight. A positive correlation was also observed between the Hg^0 and Hg^{2+} volatiles (**Fig. 7(b)**). In addition, released amounts of total Hg and Hg^{2+} or Hg^0 exhibit a good positive correlation (**Fig. 7(c)**). These results indicate that the higher the amount of Hg in the ore, the more Hg content to be volatilized as Hg^0 .

Next, to examine the effect of ore content on Hg volatilization, we examined the relationship between Hg volatilization and each element content, as presented in **Table 1**, and the results obtained are shown in **Fig. 8**. Although variations exist (**Fig. 8(a)**), a linear negative correlation is observed among the total Hg, Hg^0 , Hg^{2+} , and Si content in the ores. However, a curved negative correlation exists

Fig. 6. Distribution of Hg forms during TPHT. (Online version in color.)

Fig. 7. Relationship among Hg content in iron ore, released amount of total-Hg, Hg^{2+} , or Hg^0 . (Online version in color.)

Fig. 8. Relationship between gangue components and released amount of total-Hg, Hg^{2+} or Hg^0 . (a) Si content, (b) Ca content. (Online version in color.)

Fig. 9. Release profiles of total-Hg from pure Hg-compounds and mixture of Hg compound and Fe_2O_3 (a) HgCl and HgCl/ Fe_2O_3 , (b) HgCl₂ and HgCl₂/ Fe_2O_3 , (c) HgS and HgS/ Fe_2O_3 , (d) HgO and HgO/ Fe_2O_3 , and (e) HgSO₄ and HgSO₄/ Fe_2O_3 . (Online version in color.)

between the Ca content and total Hg, Hg^0 , and Hg^{2+} ; and the amount of gaseous Hg tends to decrease with increasing Ca content in the ores. Although the Si and Ca contents in the ore are overwhelmingly larger than those of Hg, the increase in the content of these species may influence Hg release. A detailed investigation on this issue is a topic for future research.

3.3. Hg Release during TPHT of Model Compounds

To investigate the volatilization form of Hg from iron ore, the total Hg evolution behavior of pure Hg compounds during TPHT is shown in Fig. 9, and the results are summarized in Table 2. The evolution of Hg from HgCl also starts above 100°C, and the evolution profile peaks at approximately 180°C and 200°C. The evolution behavior of Hg from these

two pure Hg compounds exhibits asymmetric evolution profiles. However, HgS, HgO, and HgSO₄ exhibit symmetrical profiles with peaks of Hg evolution rate at approximately 400°C, 600°C, and 700°C, respectively. The order of the evolution peak temperatures was $\text{HgCl}_2 < \text{HgCl} < \text{HgS} < \text{HgO} < \text{HgSO}_4$. This order was consistent with previous reports on the TPHT of pure Hg compound species.^{7,8,13)} In contrast, the maximum TPHT peak temperatures of HgO, HgS, and HgSO₄ in this study (Table 2) appear at higher temperatures than those of other research groups using air atmosphere;¹⁴⁻¹⁷⁾ however, the above three species were in close agreement with previous reports that adopted nitrogen atmosphere.¹⁸⁾ Although Hg-TPHT has been conducted by several researchers to investigate the morphology of Hg in samples such as coal, coal ash, and gypsum, the maximum

Table 2. Summaries for Hg-TPHT results of pure Hg compounds and physical mixture of Fe₂O₃ and pure Hg compounds.

Hg species	Pure Hg compounds				Fe ₂ O ₃ mixture	
	Present work		Ref. [19]			
	Peak temp., °C	Range, °C	Peak temp., °C	Range, °C	Peak temp., °C ^b	Range, °C
HgCl ₂	150	100–700	138±4	90–350	180 (m), 400 (s)	100–550
Hg ₂ Cl ₂	180, 200	100–600	119±9	60–250	180 (w), 350 (s)	90–450
HgO (red)	600	500–700	308±1, 471±5	200–360, 370–530	500 (s)	400–600
HgS	400	250–500	n.a. ^a	n.a. ^a	450 (m)	300–450
HgSO ₄	720	600–800	583±8	500–600	550 (m)	420–650

^a Not analysis. ^b Peak intensity Designated by Hg-TPHT: w (weak), m (medium), s (strong).

TPHT peak temperature and evolution temperature of pure Hg compound species are different.^{7–9,14,15,18–24} Previous studies investigating Hg morphology in solids derived from coal utilization and gypsum via TPHT partitioned the peaks above 600°C into HgSO₄ peaks.^{9,19} Considering the above points, the results of the TPHT in Table 2 are considered logical. It is well known that the decomposition of HgCl₂, HgCl, HgS, HgO, and HgSO₄ in air follows Eqs. (1)–(9).^{24,25}

However, the Hg elimination reaction from HgS and HgSO₄ is unclear,²⁵ and it has been reported that the HgSO₄·2HgO produced in Eq. (8) was thermally stable up to 600°C.²⁴ The complexity of the reaction may also be responsible for the different Hg-TPHT results in different research groups. Although there are some problems with the TPHT described above, the results of Hg evolution from iron ore can be compared with the results presented in Table 2, because the evolution behavior of Hg from ore and the TPHT of pure Hg compounds were carried out in the same apparatus and reaction conditions (temperature rise rate and atmosphere) in this study.

Figure 9 also presents the results of Hg evolution from a mixture of Fe₂O₃/Hg compounds. The evolution of Hg from HgCl/Fe₂O₃ is observed above 100°C, and the profile exhibits two peaks at 180°C and 350°C, respectively (Fig. 9(a)). Interestingly, this profile is relatively different from that of HgCl, and a new peak appears at 350°C. The evolution of Hg from HgCl₂/Fe₂O₃ is observed above 100°C. It

exhibits an asymmetric weak peak at approximately 180°C, and then decreased at 300°C. Although the evolution profile of Hg from HgCl₂ is not observed above 300°C (Fig. 9(b)), a large peak appears at approximately 420°C for the HgCl₂/Fe₂O₃ mixture. This tendency is similar to that of the HgCl/Fe₂O₃ mixture.

HgS/Fe₂O₃ exhibits a similar Hg evolution behavior to that of the pure compound. In contrast, the Hg evolution rates of HgO/Fe₂O₃ (Fig. 9(d)) and HgSO₄/Fe₂O₃ (Fig. 9(e)) exhibit symmetrical evolution profiles with velocity peaks at approximately 500°C and 550°C, respectively. The evolution behavior of Hg from the physical mixture of Hg compounds and Fe₂O₃, excluding HgS, relatively differs from that of pure Hg. In other words, two peaks are observed for Hg chloride/Fe₂O₃, and the peak temperatures of HgO and HgSO₄/Fe₂O₃ shift to lower temperatures compared to those of the pure compound. The 1st peak observed at approximately 200°C for HgCl or HgCl₂/Fe₂O₃ was derived from HgCl and HgCl₂, respectively. However, because the 2nd peak is not observed in the pure compound, it is considered to be triggered by the evolution of HgCl and HgCl₂ species interacting with Fe₂O₃ during the heating process. According to previous reports, the adsorption of gaseous Hg⁰ on Fe₂O₃ does not occur.²⁶ Therefore, the above interaction may be triggered by the solid-solid reaction between the HgCl species and Fe₂O₃. However, the peak temperatures of HgO/Fe₂O₃ and HgSO₄/Fe₂O₃ shift to lower temperatures. A similar shift of the TPHT peak was reported in a previous study of the Hg-TPHT of a mixture of various Hg compounds and some substrates (SiO₂, CaSO₄·2H₂O).²⁴ It has been speculated that the decrease in the peak temperature of the Hg evolution profile was owing to the autocatalysis reaction by the substrate.^{24,27} Therefore, the decrease in the Hg evolution peak temperature from the HgO and HgSO₄/Fe₂O₃ mixed samples may be triggered by Fe₂O₃ acting as a catalyst. The details of this discussion will be the topic for future research.

According to previous studies that investigated the behavior of Hg release from coal, bauxite, and sequential leached coal, the Hg species released at high temperatures above 600°C are those associated with silicate,^{5,6,15} montmorillonite,¹⁰ refractory silicate, and mineral matrices.¹¹ Consequently, the high-temperature Hg release observed at ≥ 600°C for all ores may be owing to the mineral matter present in ores.

3.4. Proportion of Hg Species Evolved during TPHT

Based on the results presented in Fig. 9, Fig. 10 shows the results of the curve fitting of the Hg evolution profile observed in Fig. 3. Here, $\text{HgCl}_{\text{Fe}_2\text{O}_3}$ and $\text{HgCl}_{\text{Fe}_2\text{O}_3}$ in Fig. 10 depict the Hg species that interacted with Fe_2O_3 , as shown in Fig. 9. Table 3 presents the proportion of Hg forms calculated based on the curve-fitting results. As shown in Fig. 10, the Hg species volatilized above 600°C was not identified in this study; hence, the Hg species are unknown. In the AUL, Hg species that evolved until 600°C were mainly classified as HgCl , $\text{HgCl}_{\text{Fe}_2\text{O}_3}$, HgS , and HgO . According to curve-fitting, HgS is the most abundant species, followed by unknown species, and $\text{HgCl}_{\text{Fe}_2\text{O}_3}$ species accounts for a significant proportion. In the INL, the Hg forms volatilized below 600°C are assigned to $\text{HgCl}_{\text{Fe}_2\text{O}_3}$, HgS , $\text{HgCl}_{2\text{Fe}_2\text{O}_3}$, HgO , and HgSO_4 , and the presence of HgCl_2 and HgCl species is not observed. The Hg species volatilized above 600°C were unknown species. In INL, although the presence of HgCl_2 was not observed, $\text{HgCl}_{2\text{Fe}_2\text{O}_3}$ was detected. Using the model compounds described above, $\text{HgCl}_{2\text{Fe}_2\text{O}_3}$ may be assigned as the source owing to the secondary reaction with HgCl_2 and Fe_2O_3 from the experimental results (Fig. 9). In AUH, HgCl_2 , HgCl , HgO , and HgSO_4 account for most of the volatile species below 600°C , and $\text{HgCl}_{\text{Fe}_2\text{O}_3}$, HgS , and $\text{HgCl}_{2\text{Fe}_2\text{O}_3}$ are observed in small amounts. Similar to the

INL, unknown species account for most of the volatile species. The volatile Hg species in the ISH mainly comprise HgCl , $\text{HgCl}_{2\text{Fe}_2\text{O}_3}$, HgO , and HgSO_4 , with small amounts of $\text{HgCl}_{\text{Fe}_2\text{O}_3}$ and HgS . In addition, half of the volatiles are unknown. Although unknown species account for 80% of the volatiles from BRH, the others comprise HgO and HgSO_4 . From these results, it was determined that the forms of Hg evolution below 600°C were primarily assigned to HgCl_2 and HgCl . $\text{HgCl}_{\text{Fe}_2\text{O}_3}$, HgS , $\text{HgCl}_{2\text{Fe}_2\text{O}_3}$, HgO , and HgSO_4 , and their proportions depended on the type of iron ore.

The present study simulates the desorption behavior of mercury in the sintering process of iron ore. However, in the sintering process, carbonaceous substances for combustion and materials for adjusting basicity are added to iron ore. These substances are thought to affect the mercury desorption from iron ore during heating treatment. In the future, it will be important to study the mixture of iron ore with carbonaceous and basicity adjustment substances.

4. Conclusions

This study is focused on the determination of Hg release forms and profiles from iron ore during temperature-programmed heat treatment. The evolution behavior of Hg in

Fig. 10. Proportion of the Hg species that evolved during TPHT. (a) AUL, (b) INH, (c) AUH, (d) ISH, and (e) BRH. (Online version in color.)

Table 3. Summary of information in Fig. 9 and proportion of Hg forms.

Sample	Proportion of Hg evolution form, %-evolution basis							
	HgCl_2	HgCl	$\text{HgCl}_{\text{Fe}_2\text{O}_3}$	HgS	$\text{HgCl}_{2\text{Fe}_2\text{O}_3}$	HgO	HgSO_4	Unknown
AUL	2	9	16	36	0	5	3	29
INH	0	0	3	3	5	3	16	70
AUH	3	5	1	1	1	4	5	80
BRH	1	0	1	0	2	7	11	78
ISH	0	17	2	2	9	13	7	50

iron ores depends on the type of iron ore. The Hg species that evolved during the heating treatment consisted of both Hg^0 and Hg^{2+} .

When the physical mixture of HgCl or HgCl_2 and Fe_2O_3 was heated, the evolution profile showed that in addition to the evolution peak when the pure mercury chloride species was solely THTP, owing to a secondary reaction, a new evolution peak emerged on the high-temperature side. In the case of the physical mixture of HgO or HgSO_4 and Fe_2O_3 , the Hg evolution peak observed in the pure compounds shifted to the lower temperature side. The curve-fitting of Hg evolution behavior for iron ore indicated that the Hg species that evolved below 600°C were chlorides, sulfide, sulfate, and oxide species. However, the Hg species that evolved at temperatures above 600°C , which account for most of the desorbed Hg in several ores, were unknown.

Supporting Information

Figure S1 in Supporting Information is apparatus of Temperature-Programmed Heat Treatment.

This material is available on the Journal website at <https://doi.org/10.2355/isijinternational.ISIJINT-2021-295>.

Acknowledgments

This study was supported in part by a Grant-in-Aid for Challenging Research (Exploratory) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, by the Iron and Steel Institute of Japan (ISIJ), and by the Steel Foundation for Environmental Protection Technology (SEPT).

REFERENCES

- 1) P. Charvát, L. Klimeš, J. Pospíšil, J. J. Klemesš and P. S. Varbanov: *J. Clean. Prod.*, **267** (2020), 122087. <https://doi.org/10.1016/j.jclepro.2020.122087>
- 2) L. B. Clarke and L. L. Sloss: Trace Elements - Emissions from Coal Combustion and Gasification, IEACR/49, IEA Coal Research, London, (1992), 15.
- 3) M. Takaoka, K. Shiota and T. Kusakabe: Report of the Steel Foundation for Environmental Protection Technology (SEPT), SEPT, Tokyo, (2006).
- 4) AMAP and UN Environment: Technical Background Report for the Global Mercury Assessment 2018, Arctic Monitoring and Assessment Programme and UN Environment Programme, Chemicals and Health Branch, Tromsø and Geneva, (2019).
- 5) S. Guo, J. Yang and Z. Liu: *Energy Fuels*, **23** (2009), 4817. <https://doi.org/10.1021/ef9002395>
- 6) S. Guo, J. Yang and Z. Liu: *Energy Fuels*, **26** (2012), 3388. <https://doi.org/10.1021/ef201598d>
- 7) M. A. Lopez-Anton, Y. Yuan, R. Perry and M. M. Maroto-Valer: *Fuel*, **89** (2010), 629. <https://doi.org/10.1016/j.fuel.2009.08.034>
- 8) M. Rumayor, N. Fernandez-Miranda, M. A. Lopez-Anton, M. Diaz-Somoano and M. R. Martinez-Tarazona: *Fuel Process. Technol.*, **132** (2015), 9. <https://doi.org/10.1016/j.fuproc.2014.12.032>
- 9) M. Rumayor, M. Diaz-Somoano, M. A. Lopez-Anton and M. R. Martinez-Tarazona: *Chemosphere*, **119** (2015), 459. <https://doi.org/10.1016/j.chemosphere.2014.07.010>
- 10) L. Gao, Y. Wang, Q. Huang and S. Guo: *Fuel*, **200** (2017), 22. <https://doi.org/10.1016/j.fuel.2017.03.045>
- 11) P. Xu, B. Zhang, X. Zeng, Y. Xu, G. Luo and H. Yao: *Int. J. Coal Geol.*, **170** (2017), 14. <https://doi.org/10.1016/j.coal.2016.08.023>
- 12) N. Tsubouchi, Y. Mochizuki, Y. Ono, K. Uebo, T. Takanohashi and N. Sakimoto: *ISIJ Int.*, **54** (2014), 2439. <https://doi.org/10.2355/isijinternational.54.2439>
- 13) X. Liu, S. Wang, L. Zhang, Y. Wu, L. Duan and J. Hao: *Fuel*, **111** (2013), 621. <https://doi.org/10.1016/j.fuel.2013.03.052>
- 14) S.-K. Back, D. Bhatta, S.-H. Kim, H.-N. Jang, J.-H. Kim, K.-H. Kim, Y.-R. Kim and Y.-C. Seo: *J. Mater. Cycles Waste Manag.*, **20** (2018), 622. <https://link.springer.com/article/10.1007/s10163-017-0630-4>
- 15) T. Zhao, X. Wang, X. Yang, X. Yan, Z. Nie and Q. Huang: *J. Mater. Cycles Waste Manag.*, **19** (2017), 712. <https://link.springer.com/article/10.1007/s10163-016-0468-1>
- 16) S. A. Tariq and J. O. Hill: *J. Therm. Anal.*, **21** (1981), 277. <https://link.springer.com/article/10.1007/BF01914211>
- 17) W. W. Wendlandt: *Thermochim. Acta*, **10** (1974), 101.
- 18) Z. Zhu, Y. Zhuo, Y. Fan and Z. Wang: *J. Environ. Sci.*, **43** (2016), 169. <https://doi.org/10.1016/j.jes.2015.09.011>
- 19) M. Rumayor, M. Diaz-Somoano, M. A. López-Antón, R. Ochoa-González and M. R. Martínez-Tarazona: *Fuel*, **148** (2015), 98. <https://doi.org/10.1016/j.fuel.2015.01.101>
- 20) M. A. Lopez-Anton, R. Perry, P. Abad-Valle, M. Díaz-Somoano, M. S. Martínez-Tarazona and M. M. Maroto-Valer: *Fuel Process. Technol.*, **92** (2011), 707. <https://doi.org/10.1016/j.fuproc.2010.12.002>
- 21) M. Pavlin, A. Popović, R. Jačimović and M. Horvat: *Open Chem.*, **16** (2018), 544. <https://doi.org/10.1515/chem-2018-0046>
- 22) M. Rumayor, M. Diaz-Somoano, M. A. Lopez-Anton and M. R. Martinez-Tarazona: *Talanta*, **114** (2013), 318. <https://doi.org/10.1016/j.talanta.2013.05.059>
- 23) D. Saniewska and M. Beldowska: *Talanta*, **168** (2017), 152. <https://doi.org/10.1016/j.talanta.2017.03.026>
- 24) M. Sedlar, M. Pavlin, A. Popović and M. Horvat: *Open Chem.*, **13** (2015), 404. <https://doi.org/10.1515/chem-2015-0051>
- 25) S. Wu, M. A. Uddin, S. Nagano, M. Ozaki and E. Sasaoka: *Energy Fuels*, **25** (2011), 144. <https://doi.org/10.1016/j.fuel.2013.07.021>
- 26) T. Liu, L. Xue, X. Guo and C.-G. Zheng: *Fuel*, **115** (2014), 179.
- 27) B. V. L'vov: *Thermochim. Acta*, **333** (1999), 21. [https://doi.org/10.1016/S0040-6031\(99\)00086-6](https://doi.org/10.1016/S0040-6031(99)00086-6)