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RESEARCH ARTICLE

Volatilization Behavior of Arsenic from a Hematite Ore During Non-isothermal Heating in Argon Atmosphere

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Abstract

Due to the increase in steel production in the world and the depletion of high-grade ore resources, there is a need to investigate the use of low-grade ores that includes arsenic-containing iron ores. Arsenic (As) is volatile, and As removal from the ore by roasting or sintering is limited because of many chemical interactions with other metallic elements within the ore. In this experiment, arsenic volatilization was thermodynamically investigated and the volatilization characteristic from a hematite ore in argon atmosphere was investigated in the temperature range of 298–1623 K using the thermogravimetric-differential scanning calorimetry (TG-DSC) and the vertical tube furnace. The percentage weight loss and volatilization rate were evaluated by raising the temperature non-isothermally at 10 K/min in the TG-DSC and the vertical tube furnace in an argon atmosphere. X-ray diffraction (XRD) analyses were done on the cooled and crushed samples to identify the change in phases after heating to temperatures above 1273 K. Electron probe microanalysis analyses were used to verify the possibility of existence of some of the phases identified by XRD. The results showed that the percentage weight loss of the pellet increased with increase in temperature. Metallic element distribution after non-isothermal heating to temperatures above 1273 K showed that As was likely to be highly concentrated in the same area as Ca, Si, and Al. This was in agreement with the XRD results and the thermodynamic predictions, which showed that $3CaO{\cdot}2As_2O5(s)$ and the $AlAsO4(s)$ were likely to be the most stable As-containing phases even at temperatures of about 1623 K. The volatilization of all volatile material from the ore depends on the bonding energy holding the volatile matter in the pellet.

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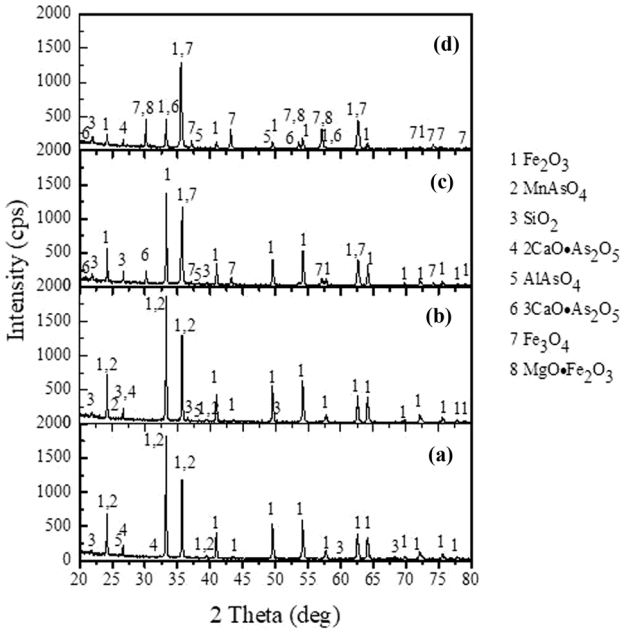
Graphical Abstract



Keywords Arsenic volatilization · Percentage weight loss · Volatilization rate · Sintering · Non-isothermal heating

Abbreviations

ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
XRD	X-ray diffraction
LOI	Loss on ignition
XRF	X-ray fluorescence

Introduction

The rapid growth in steel industry has triggered the increase in raw material demand. High-grade iron ore reserves have been depleted leaving researchers with big responsibility to look for alternative raw materials to sustain the steel industry. The effective utilization of these alternative ores has some economic advantages. Prices of such ores are still low because there is little or no competition in the demand for this resource.

Existing alternative resources include iron ores with high levels of Arsenic (As). The mode of occurrence of As in these ores is difficult to know because of a wide range of arsenates and associated minerals that As can form. Furthermore, some As compounds show some polymorphic behavior like $As_2O_3(s)$ which can exist as arsenolite, claudetite, or a glassy form [1]. Compounds of As have oxidation states ranging from +2, +3, and +5; hence, As can exist as arsenopyrite ($Fe_xAs_yS_z(s)$), oxides ($As_2O_5(s)$ or $As_2O_3(s)$) or sulfides ($As_2S_3(s)$) in ores [2, 3]. Arsenic content in iron ore can be as high as 0.5 wt% [4]. If ores with As are directly charged into the blast furnace, As readily dissolves into the molten iron. Removal of the As from molten iron is extremely difficult, finding its way into steel, thereby badly affecting the mechanical properties of steel products. Engineers demand those steels for special purposes like that used in petroleum bars, large dynamo rotor and in nuke industries contains no As [5]. Methods of removing As prior to the blast furnace should be developed in order to fully utilize these ores.

Due to the volatile properties of As, many researchers have tried to remove As by roasting or sintering, but the methods they suggested were not effective enough as 50–75% of the As was retained inside the treated ore [6]. The vapors or gases produced during the roasting or sintering of As-containing ores are toxic and associated with a lot of environmental pollution. Chakraborti et al. [6] investigated the Fe–As–S–O system in inert, oxidizing and reducing atmospheres at 798 K and 873 K. They used predominance diagrams to explain their findings and showed that stability of As phases and gaseous compounds varied with the partial pressures of $O_2(g)$, $S_2(g)$, and $As_4(g)$.

Contreras et al. [7] used HSC chemistry 5.0 software to predict the trace elements distribution between gas, liquid, and solid phases as a function of temperature in coal combustion. They found that $3CaO{\cdot}As_2O_5(s)$ was the most stable phase and remains non-volatile even at temperatures above 1573 K. In addition, the solubility of $3CaO{\cdot}As_2O_5(s)$ in water is low. Lui et al. [4] investigated As volatilization during coal combustion based on isothermal thermogravimetric analysis at 873–1773 K. They

plotted the derivative of the mass loss curve of As with respect to temperature and showed that As volatilization was strongly related to the chemical bonds holding As in the coal.

The behavior of As in iron ores during sintering is yet to be cleared because of the complexity of the existence of the As in the ore and also the standard gas for calibrating state of the art equipment like the Quadrupole Mass spectrometer (QMS) is not easily available. Furthermore, As forms many complex compounds with various metallic elements within the ores during sintering. Clarification of the pollution prevention mechanism caused by the treatment of As-containing ores also demands great attention. The current research aims to better understand how the arsenic-containing hematite ore will behave during non-isothermal heating in an Ar atmosphere and to find the stable As-containing phases formed after heating the hematite ore to temperatures in the range of 298–1623 K using the TG-DSC and the vertical tube furnace. The phases formed after heating the hematite ore were then analyzed using the XRD, and verification of the existence of some of the phases identified was done using some EPMA mappings. The Ar atmosphere was used to provide the basic information on the interactions occurring within the ore with minimum interference from the gaseous atmosphere around the sample used in the actual sintering process. But, first, thermodynamic analyses of the As compounds that may be found during the sintering process were done. This investigation might help in understanding of some of the phases that might develop during sintering of the hematite ore-containing As, and to develop the technology of preventing the pollution caused by As as well as to find the most suitable temperature to remove most of the As from the ore.

Thermodynamics of Natural Arsenic Compounds

The mode of occurrence of As in the iron ore is difficult to know because of the wide range of compounds that As can form with other associated compounds in the ore. Arsenic has atomic number of 33 and belong to group 15 on the periodic table. As can have oxidation state from + 2, + 3, and + 5, hence, As can exist in the form of an oxide, sulfide, or arsenopyrite.

Arsenic Oxides

The known stable As oxides are $As_2O_3(s)$ and $As_2O_5(s)$ [8]. The available data on the thermal stability of these oxides are contradictory because $As_2O_3(s)$ shows some polymorphic behavior. $As_2O_3(s)$ can exist in three major forms. These are the arsenolite, clauditite, and the glass form [1]. The arsenolite has a cubic structure and was reported to be stable at temperatures below 506 K. Arsenolite was reported to be composed of As_2O_3 dimers, As_4O_6. Above 506 K, the claudetite form, which is monoclinic, is stable. The claudetite form was reported to exist in two forms, which are the claudetite I and II. The transformation of the arsenolite to the clauditite was reported to be very slow. The Gibbs free energies of formation of arsenolite and claudetite are shown as follows [1]:

$$2As(s) + 3/2O_2(g) = As_2O_3(s, \text{arsenolite}), \tag{1}$$

$$\Delta G^\circ = -647,650 - 36.9T + 123.5T\log T - 0.10 \times 10^{-3}T^2 - 125.4 \times 10^3 T^{-1}(\text{J/mol})(278-551\ \text{K}) \tag{2}$$

$$2As(s) + 3/2O_2(g) = As_2O_3(s, \text{claudetite}), \tag{3}$$

$$\Delta G^\circ = -630,500 - 71.0T + 123.5T\log T - 0.10 \times 10^{-3}T^2 - 125.4 \times 10^3 T^{-1}(\text{J/mol})(278-585\ \text{K}). \tag{4}$$

The Gibbs free energy for the transformation of the arsenolite to the claudetite form can be shown as follows:

$$2As_2O_3(s, \text{arsenolite}) = 2As_2O_3(s, \text{claudetite}), \tag{5}$$

$$\Delta G^\circ = 34,300 - 68.2T\ (\text{J/mol}). \tag{6}$$

From Eq. (6), the transformation temperature was estimated to be around 503 K; however, water vapor was reported to accelerate this transformation at around 453 K.

The previous research [1] estimated the decomposition vapor pressures of $As_2O_3(s$, arsenolite) and $As_2O_3(s$, claudetite). The vapor pressures were expressed using the following equations [1]:

$$2As_2O_3(s, \text{arsenolite}) = As_4O_6(g), \tag{7}$$

$$\log p = \frac{-6670}{T} + 10.81(\text{atm}), \tag{8}$$

$$2As_2O_3(s, \text{claudetite}) = As_4O_6(g), \tag{9}$$

$$\log p = \frac{-4873}{T} + 7.26(\text{atm}). \tag{10}$$

Combination of Eqs. (8) and (10) shows that the transformation from arsenolite ($As_2O_3(s$, arsenolite)) to claudetite ($As_2O_3(s$, claudetite)) is accompanied by loss of arsenic in the form of $As_4O_6(g)$.

The $As_2O_3(s$, glass) form was reported to be formed by slow condensation of the gaseous $As_2O_3(g)$ at temperatures

of above 523 K. Exposing the $As_2O_3(s$, glass) to air transforms the $As_2O_3(s$, glass) to the $As_2O_3(s$, arsenolite) form.

The $As_2O_5(s)$ can be decomposed by either dissociative or non-dissociative decomposition according to the equations as follows [6, 9]:

$$2As_2O_5(s) = As_4O_6(g) + 2O_2(g), \tag{11}$$

$$\Delta G^{\circ} = 581,481.16 - 563.02T(810-1013\,\mathrm{K}), \tag{12}$$

Or

$$2As_2O_5(s) = As_4O_{10}(g), \tag{13}$$

$$\Delta G^{\circ} = 301,400 \pm 7.8 - 265.5 \pm 8.0T(865-1009\,\mathrm{K})\mathrm{J/mol} \tag{14}$$

Followed by dissociative disintegration in the gas phase:

$$As_4O_{(10-y)}(g) = As_4O_{(9-y)}(g) + 0.5O_2(g). \tag{15}$$

Moiseev et al. [8] performed some thermodynamic modeling of the composition of the condensed medium and the partial pressures of the gas-phase components formed on heating $As_2O_3(s)$ and $As_2O_5(s)$ from 300 K to their evaporation temperatures in argon atmosphere. The partial pressures of the gaseous compounds from the decomposition of $As_2O_3(s)$ were temperature dependent. The partial pressures variations were represented by the following equations [8]:

$$\log p(O_2) = 3.5 - 9740/T(300-1010\,\mathrm{K}), \tag{16}$$

$$\log p(\mathrm{AsO}) = 9.0368 - 15,697/T(300-1010\,\mathrm{K}), \tag{17}$$

$$\log p(AsO_2) = 4.4846 - 15,335/T(300-1010\,\mathrm{K}), \tag{18}$$

$$\log p(As_4O_6) = 6.4534 - 5387/T(300-500\,\mathrm{K}), \tag{19}$$

$$\log p(As_4O_7) = 4.558 - 7238/T(300-500\,\mathrm{K}), \tag{20}$$

$$\log p(As_4O_8) = 1.3342 - 9525/T(300-650\,\mathrm{K}). \tag{21}$$

From the above information, it was concluded that the main equation for the decomposition of $As_2O_3(s)$ was

$$2As_2O_3(s) = As_4O_6(g). \tag{22}$$

Moiseev et al. [8] also showed that the partial pressure of the possible gaseous components in $As_2O_5(s)$ decomposition follows the following order:

$$p(As_4O_{10}(g)) > p(As_4O_8(g)) > p(As_4O_7(g)) > p(As_4O_9(g)) > p(As_4O_6g)) > p(AsO_2(g)) > p(AsO(g)).$$

The following equations describes the temperature-dependent partial pressure variations of the gaseous component observed in the decomposition of $As_2O_5(s)$ [8]:

$$\log p(O_2) = 6.171 - 7635/T(358-970\,\mathrm{K}), \tag{23}$$

$$\log p(\mathrm{AsO}) = 10.42 - 20,635/T(713-970\,\mathrm{K}), \tag{24}$$

$$\log p(AsO_2) = 10.775 - 19,264/T(630-970\,\mathrm{K}), \tag{25}$$

$$\log p(As_4O_6) = 15.5067 - 18,833/T(532-880\,\mathrm{K}), \tag{26}$$

$$\log p(As_4O_7) = 15.245 - 17,476/T(532-880\,\mathrm{K}), \tag{27}$$

$$\log p(As_4O_8) = 14.55 - 16,875/T(532-880\,\mathrm{K}), \tag{28}$$

$$\log p(As_4O_9) = 13.518 - 17,042/T(532-880\,\mathrm{K}), \tag{29}$$

$$\log p(As_4O_{10}) = 12.2366 - 13,035/T(532-880\,\mathrm{K}). \tag{30}$$

Based on the data above, Eq. (13) is reported to be the main reaction in the $As_2O_5(s)$ decomposition.

Arsenic Sulfides

The following arsenic sulfides were reported to exist in the form of $As_4S_3(s)$, $As_4S_4(s)$, $As_2S_3(s)$, and $As_2S_5(s)$ [6]. $As_4S_4(s)$, realgar, can have both α and β structures. The $As_2S_3(s)$ is the orpiment. The $As_4S_3(s)$, dimorphite, is very unstable. The gaseous products from the vaporization of $As_2S_3(s)$ were reported to contain $As_4S_4(g)$, $As_2S_2(g)$, $AsS(g)$, $S_2(g)$, and $As_2S_3(g)$ at about 465 K [10]. The overall reaction of $As_2S_3(s)$ decomposition was represented as follows:

$$As_2S_3(s) = {}^{2}/_{n}As_nS_n(g) + {}^{1}/_{2}S_2(g) \quad \text{were } n = 1-4. \tag{31}$$

Hence, the primary vaporization reaction for $As_2S_3(s)$ was reported to follow Eqs. (32) and (33):

$$As_2S_3(s) = As_2S_3(g), \tag{32}$$

$$As_2S_3(s) = {}^{1}/_{2}As_4S_4(g) + {}^{1}/_{2}S_2(g), \tag{33}$$

with a little amount of $As_2S_3(s)$ decomposing following Eq. (34):

$$As_2S_3(s) = {}^{1}/_{2}As_4S_5(g) + {}^{1}/_{4}S_2(g). \tag{34}$$

Equations (32) and (33) are reported to be the predominant reactions in the decomposition of $As_2S_3(s)$ [10].

Arsenopyrite

The arsenic in iron ore can also exist in the form of an arsenopyrite, $Fe_xAs_yS_z(s)$. The $Fe_xAs_yS_z(s)$ was found to decompose on heating in oxygen atmosphere at around 923 K, and the suggested decomposition reaction follows Eq. (35) [11]:

$$Fe_xAs_yS_z(s) = Fe_xS_y(s) + yAs(g). \quad (35)$$

The $Fe_xS_y(s)$ was reported to be pyrrhotite, ($Fe_{(1-x)}S$ (*s*) (x=0–0.2)). $FeS_2(s)$ or $FeAs_2(s)$ were also reported to be the product of $Fe_xAs_yS_z(s)$ decomposition. The reaction product for the decomposition of arsenopyrite depends on the initial composition of $Fe_xAs_yS_z(s)$. Arsenopyrite decomposition was reported to occur in inert atmosphere at a temperature range of 723–973 K [11].

Interactions of As with Metallic Components

Volatilization of As from iron ore during sintering or roasting can be complicated by interactions with other metal components in the ore. The possible compounds formed by these interactions include $FeAsO_4(s)$, $AlAsO_4(s)$, $KAs_3O_4(s)$, $NaAs_3O_8(s)$, $3MgO{\cdot}As_2O_5(s)$, and $CaO{\cdot}As_2O_5(s)$ [2, 4, 7, 11]. The common sinter phases formed with $CaO(s)$ during sintering are $CaO{\cdot}Fe_2O_3(s)$ and $2CaO{\cdot}SiO_2(s)$. By the plot of ΔG° vs temperature, Fig. 1, using the thermodynamic data of Eqs. (36) to (44) as follows [6, 12]:

$$CaO(s) + Fe_2O_3(s) = CaO \cdot Fe_2O_3(s), \quad (36)$$

$$\Delta G^\circ = -30,000 - 4.8T(973 - 1489\,\mathrm{K})\mathrm{J/mol}, \quad (37)$$

$$2CaO(s) + Fe_2O_3(s) = 2CaO \cdot Fe_2O_3(s), \quad (38)$$

$$\Delta G^\circ = -53,100 - 2.5T(973 - 1723\,\mathrm{K})\mathrm{J/mol}, \quad (39)$$

$$2CaO(s) + SiO_2(s) = 2CaO \cdot SiO_2(s), \quad (40)$$

$$\Delta G^\circ = -120,000 - 11.3T(298 - 2403\mathrm{K})\mathrm{J/mol}, \quad (41)$$

$$Al_2O_3(s) + As_2O_3(g) + O_2(g) = 2AlAsO_4(s), \quad (42)$$

$$\Delta G^\circ = -536,068 + 93.49T(1373{-}1673\mathrm{K})\mathrm{J/mol}, \quad (43)$$

$$3CaO(s) + As_2O_3(g) + O_2(g) = 3CaO \cdot 2As_2O_5(s), \quad (44)$$

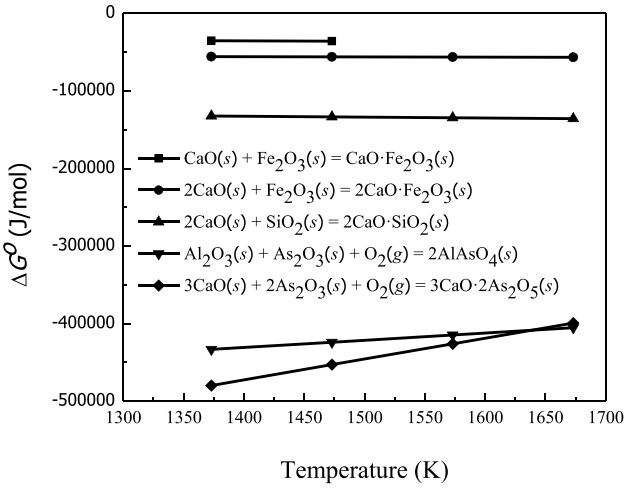


Fig. 1 Plot of ΔG° vs temperature for some of the possible reactions that can occur during sintering

$$\Delta G^\circ = -775,454 + 268.8T(1373{-}1678\mathrm{K})\mathrm{J/mol}, \quad (45)$$

$$3As_4O_6(g) + 7O_2(g) + 4Fe_3O_4(s) = 12FeAsO_4(s), \quad (46)$$

$$\Delta G^\circ = -3.24 \times 10^6 + 2240.76T\log T + 1563.36T - 2.29 \times 10^{-2}T^2\mathrm{J/mol}. \quad (47)$$

The ΔG° for Eqs. (42) and (44) were calculated using FactSage 6.2 software. It was concluded from Fig. 1 that formation of the $3CaO{\cdot}2As_2O_5(s)$ and $2AlAsO_4(s)$ at the selected temperature range is highly favored than the calcium ferrite and the $2CaO{\cdot}SiO_2(s)$.

Experimental

Materials

Reagent grade $As_2O_3(s)$ was added to an As-containing hematite ore with As content of 0.035 wt%, loss on ignition (LOI) of 7.10 wt% and average particle size of under 1 mm. The mixture was blended at 34 rpm for 1 h using the Turbula Mixer (T_2F Nr. 120942 Switzerland) to make a blend of chemical composition shown in Table 1.

The As content in the blend was measured using the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and found to be 0.74 wt%. For a general understanding of the other components in the ore, X-ray fluorescence (XRF) analysis was done on the ore. The other components include $TiO_2(s)$, $Cr_2O_3(s)$, $NiO(s)$, $P_2O_5(s)$, and $Na_2O(s)$. The phases in the hematite ore-As_2O_3 blend were identified by X-ray diffraction (XRD) (Bruker AXS) with a Cu tube at a scan angle of 20°–80°, scanning rate of 2°/min,

Table 1 Chemical composition of hematite ore-As_2O_3 blend (wt%)

Analyte	Total Fe	FeO	Fe_2O_3	SiO_2	Al_2O_3	CaO	S	K	MgO	MnO	As	LOI	Others
Fe_2O_3 ore-As_2O_3 blend	54.36	0.25	77.45	6.08	1.59	0.36	0.07	0.01	0.09	0.42	0.74	9.49	12.94

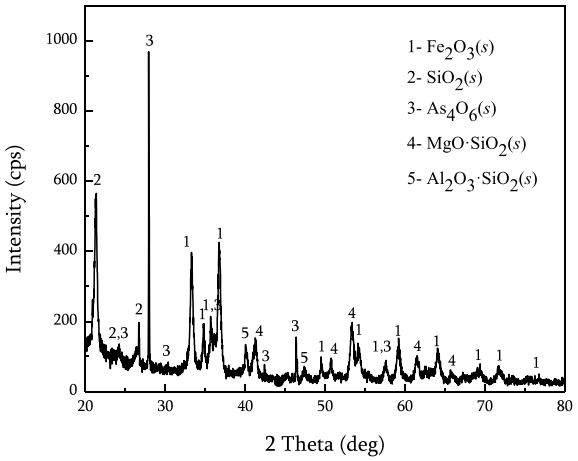


Fig. 2 XRD pattern of the hematite ore-As_2O_3 blend

a voltage of 40 kV, and a current of 40 mA. The results are as shown in Fig. 2.

The Fe-containing phase identified in the hematite ore-As_2O_3 blend was the $Fe_2O_3(s)$. As existed as the $As_2O_3(s)$ dimer, $As_4O_6(s)$ in the blend. The gangue components in the ore were the $SiO_2(s)$, $MgO{\cdot}SiO_2(s)$, and $Al_2O_3{\cdot}SiO_2(s)$.

Experimental Procedure

Mass Change Profile Based on the TG-DSC

The mass loss profile in the ores was determined by the TG-DSC (TGA/DSC 1 Star system Mettler Toledo). About 100 mg of the hematite ore only and the hematite ore-As_2O_3 blend of particle size, under 1 mm were placed in an aluminum oxide crucible (7 mm ID × 8 mm OD × 4.5 mm Height). The crucible with the sample was placed into the TG-DSC furnace. Temperature was raised from 298 to 1573 K at a rate of 10 K/min in argon atmosphere. The gas flow rate was 70 mL/min of Ar gas.

Mass Loss Profile Based on the Vertical Tube Furnace

The ore of particle size of under 1 mm was pressed at 20 MPa into cylindrical disk pellets weighing 1 g and air-dried for 24 h. Two pellets with total mass of 2 g were placed into a platinum crucible (basket) and suspended in the vertical tube furnace using a platinum wire. Temperature was raised at 10 K/min to target temperature in an Ar atmosphere at 1 L/min. When the target temperature ranging from 298 to 1623 K was reached, the crucible was pulled to the cold end of the furnace and cooled to room temperature in Ar atmosphere. After cooling, the final mass of the pellets was measured. This procedure was repeated at least three times, and the average final weight was calculated and used in the subsequent calculations.

The hematite ore-As_2O_3 blend was also pressed at 20 MPa into a cylindrical disk weighing about 1 g. Two disks from the hematite ore-As_2O_3 blend weighing about 2 g were placed into the platinum crucible (basket) and suspended in the vertical tube furnace using a platinum wire. Temperature was raised at 10 K/min to target temperature in an Ar atmosphere at 1 L/min. When the target temperature ranging from 298 to 1623 K was reached, the crucible was pulled to the cold end of the furnace and cooled to room temperature in Ar atmosphere. Pellets heated to temperatures above 1273 K were crushed to fine powder and supplied for XRD. The mass loss results were compared with the mass loss obtained using the hematite ore pellets and that obtained using the TG-DSC.

The percentage mass loss of all volatile matter from the pellet was evaluated using the equation:

$$\text{Percentage mass loss, } \Delta W(\%) = \frac{W_1 - W_2}{W_1} \times 100, \tag{48}$$

where W_1 is the initial mass of the pellet (g) and W_2 is the final mass of the pellet (g). The mass loss rate after heating, v (%/K) was evaluated as follows [4]:

$$v = \frac{\mathrm{d}(100 - \Delta W)}{\mathrm{d}T} = -\frac{\mathrm{d}\Delta W}{\mathrm{d}T} = -\frac{(\Delta W_{2-}\Delta W_1)}{T_2 - T_1}, \tag{49}$$

where T is the temperature (K).

To verify the possibility of existence of some of the phases identified by X-ray diffraction (XRD; Bruker AXS) analyses, electron probe microanalysis (EPMA; Joel Japan/JXA-8530F) was done on the heated, mounted, and polished hematite ore pellets. Pellets non-isothermally heated at 10 K/min to a temperature range of between 1273 and 1623 K were prepared for EPMA analyses. Temperatures above 1273 K were selected for EPMA analyses to avoid complication in the EPMA because above this temperature, the strength of the bonding phase holding the heated pellets was strong enough to prevent generations of some fines inside EPMA during the analyses. Elemental

mapping by EPMA analyses was done using a voltage of 20 keV and a beam current of 50 nA.

Results and Discussion

Percentage Mass Loss with Increasing Temperature

The mass loss profiles of the hematite ore and of the hematie-As_2O_3 blend were measured using the TG-DSC by raising the temperature at a heating rate of 10 K/min from 298 to 1623 K in an Ar atmosphere. Figure 3a and b shows the percentage mass loss from the pellet with increasing temperature based on the TG-DSC method.

The mass loss curve from the hematite ore and the hematite ore-As_2O_3 blend showed a similar trend. The change in mass was from the volatilization of all the volatile matter in the ores. The only difference was that mass loss curve shown in Fig. 3b had a higher amount of volatiles than that in Fig. 3a, which might be attributed to the presence of the As_2O_3 since the mass loss curve from the hematite ore alone was used as the baseline. In addition, the loss on ignition (LOI) of the hematite ore was determined to be 7.10 wt% while that of hematite-As_2O_3 was 9.49 wt%. The difference of about 2.39 wt% and part of this might be from the volatilized As_2O_3. The percentage weight loss curves based on the vertical tube furnace in Fig. 4 showed some similarities with that obtained from the TG-DSC data shown in Fig. 3. Thus, the change in phases from data based on the TG-DSC might be investigated using samples heated non-isothermally in the vertical tube furnace and quenched to room temperature in Ar atmosphere.

The percentage mass loss from the pellet increased with increasing temperature shown in Fig. 3a and b. The mass changes might be related to the volatilization rate and the bonding strength holding the volatile material in the pellet.

Volatilization Rate with Increase in Temperature

The volatilization rate curve was plotted by taking the derivative of the mass loss change curve shown in Fig. 3a and b. These curves helped to explain the changes in mass loss from the pellet. Based on the volatilization rate curves shown in Fig. 3a and b, some specific peaks at 473–673 K, 700–800 K, 1000–1100 K, and above 1400 K characterized the volatilization rate curves of both the hematite ore and the hematite ore-As_2O_3 blend. This showed that the volatilization of the volatile matter from the ore depends on the chemical bonds holding them in the ore. This observation was in good agreement with the findings of Lui et al. [4]

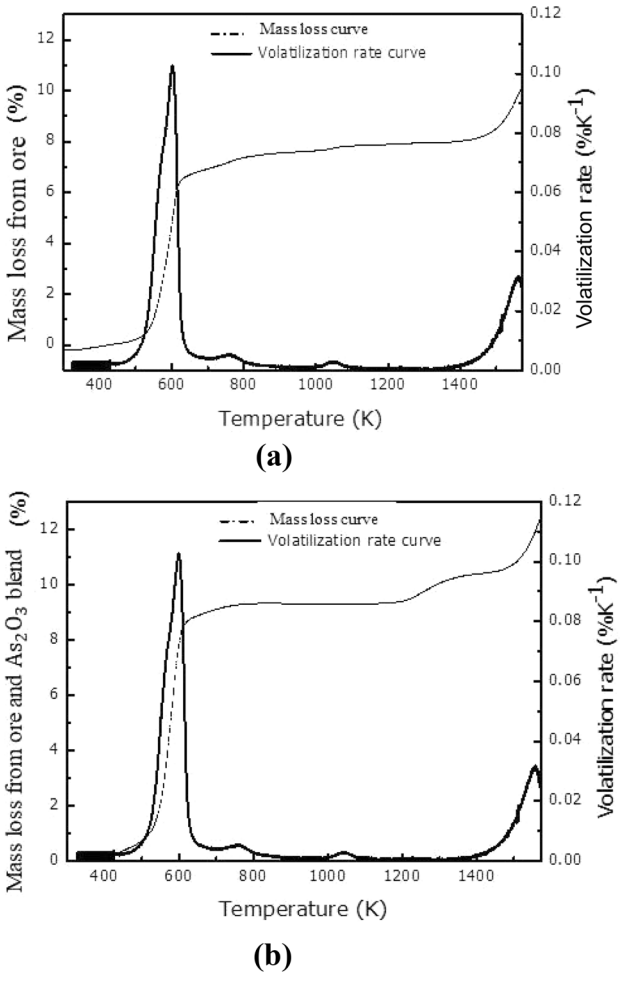


Fig. 3 Plot of mass loss and volatilization rate with increasing temperature-using data from TG-DSC of: **a** hematite ore only and **b** hematite ore-As_2O_3 blend

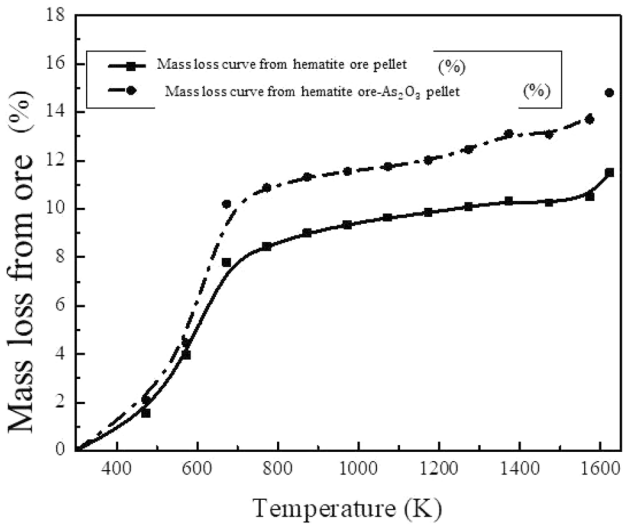


Fig. 4 Plot of mass loss with increasing temperature using data based on the vertical tube furnace

It is believed that the characteristic peak at 473–673 K in Fig. 3a might be due to dehydration of the ore while that in Fig. 3b might be due to dehydration along with the As lost from the phase transformation of $As_2O_3(s)$ shown by Eq. (5). Thermodynamic data of the phase transformation of $As_2O_3(s)$, Eq. (6) shows that the temperature of $As_2O_3(s)$ phase transformation can be estimated to be around 503 K. This phase transformation temperature was reported to be decreased to 453 K by the presence of water vapor [1]. Combination of Eq. (8) and Eq. (10) shows that the phase transformation of $As_2O_3(s)$ can be accompanied by loss of As in the form of $As_4O_6(g)$. Furthermore, the sublimation temperature of $As_2O_3(s)$ was reported to be around 588 K [13].

To provide more evidence, the TG-DSC analysis of the $As_2O_3(s)$ reagent grade was done as shown in Fig. 5.

Mass loss from the $As_2O_3(s)$ in Fig. 5 started at around 503 K that might correspond to the phase change of the $As_2O_3(s)$. This mass change increased rapidly up to temperatures of just above 600 K. This acceleration in mass loss might have been caused by the sublimation of $As_2O_3(s)$ that was reported to occur at around 588 K [13].

At 700–800 K, part of the mass loss of the hematite ore in Fig. 3b might have been from the evaporation of the remaining $As_2O_3(s)$ among other reactions. Since the boiling temperature of $As_2O_3(s)$ was reported to be around 703 K [13], Fig. 5 shows a peak between 700 and 800 K that might correspond to the evaporation of the $As_2O_3(s)$.

It was believed that the increase in volatilization rate observed above 1400 K shown in Fig. 3a and b might be due to the loss of $O_2(g)$ from the thermal decomposition of hematite, which is believed to occur above 1473 K [14]. The thermal decomposition of hematite can occur according to the equation below [12]:

$$3Fe_2O_3(s) = 2Fe_3O_4(s) + 1/2O_2(g), \tag{50}$$

$$\Delta G^\circ = 238,800 - 138.5T(298-1735\text{K})(\text{J/mol}). \tag{51}$$

The previous research [14, 15] showed that hematite decomposition increases fast at temperatures above 1473 K. The volatilization of As from the decomposition of arsenates other than $3CaO{\cdot}As_2O_5(s)$, $2CaO{\cdot}As_2O_5(s)$, and $AlAsO_4(s)$ is also expected above 1373 K. These are the reasons believed to be the cause for the increase in weight loss observed above 1400 K in Fig. 3b.

Phase Change with Increasing Temperature

During iron ore sintering, the phases formed at temperatures of above 1373 K are of major interest. The possible stable phases formed above 1373 K were investigated using XRD and the results are as shown in Fig. 6a–d.

The phases identified at 1373 K and 1473 K were $Fe_2O_3(s)$, $SiO_2(s)$, $MnAsO_4(s)$, $2CaO{\cdot}As_2O_5(s)$, and $AlAsO_4(s)$ shown in Fig. 6a, b. When the temperature was increased to 1573 K as shown in Fig. 6c, $MnAsO_4(s)$ decomposed and the stable phases identified were $Fe_2O_3(s)$, $Fe_3O_4(s)$, $SiO_2(s)$, $3CaO{\cdot}As_2O_5(s)$, and $AlAsO_4(s)$. The $3CaO{\cdot}As_2O_5(s)$, $2CaO{\cdot}As_2O_5(s)$, and $AlAsO_4(s)$ phases were the most stable As-containing phases at 1623 K. $MgO{\cdot}Fe_2O_3(s)$ was part of the stable phases identified at

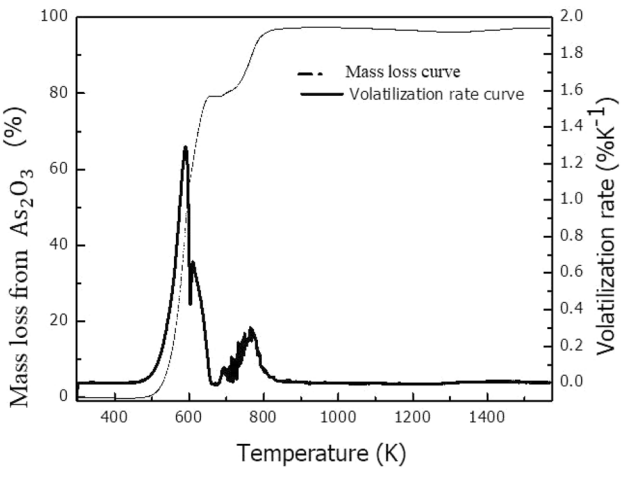


Fig. 5 Plot of mass loss and volatilization rate with increasing temperature-using data from TG-DSC of As_2O_3

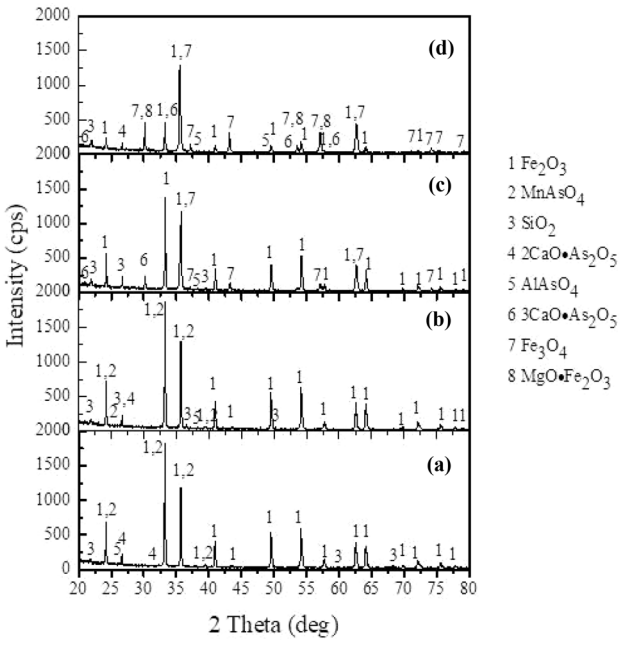


Fig. 6 XRD analysis of the hematite ore-As_2O_3 pellet after non-isothermal heating to (a) 1373 K, (b) 1473 K, (c) 1573 K, and (d) 1623 K

1623 K in Fig. 6d. It is clear from Fig. 6c, d that hematite was thermally decomposed to $Fe_3O_4(s)$ evidenced by the presence of $Fe_3O_4(s)$ peaks at 1573 K and 1623 K.

These results also showed that even though As is volatile, complete escape of the As from the ore was complicated by the presence of other metallic elements components in the ore. Just as was shown by thermodynamic calculations in Fig. 1, $3CaO{\cdot}As_2O_5(s)$, $2CaO{\cdot}As_2O_5(s)$, and $AlAsO_4(s)$ phases were the most stable As-containing phases even at 1623 K.

Elemental Distribution in the Sintered Pellets with Increasing Temperature

To provide additional evidence of the formed phases identified by XRD, EPMA (Joel JXA-8530F) mappings were performed at an acceleration voltage of 20 keV and magnification of ×400 on the heated, mounted, and polished pellets of hematite ore. In particular, EPMA analyses were done to verify that As was likely to be distributed in the hematite ore after non-isothermal heating to temperatures above 1273 K.

Figure 7a–d shows the EPMA mapping results of the hematite ore with increasing temperature and indicates that As was highly concentrated in the same area as Ca, and Al shown by the points marked in red on the EPMA mapping results. Thermodynamics shown in Fig. 1 indicate that in the presence of Ca and Al, arsenic is more likely to react with Ca and Al producing $3CaO{\cdot}2As_2O_5(s)$ and $AlAsO_4(s)$. XRD showed the presence of $2CaO{\cdot}As_2O_5(s)$, $3CaO{\cdot}As_2O_5(s)$, and $AlAsO_4(s)$ even at 1623 K. It could be concluded that $2CaO{\cdot}As_2O_5(s)$, $3CaO{\cdot}As_2O_5(s)$, and the $AlAsO_4(s)$ were likely to be the most stable As-containing phase basing on the XRD and EPMA results. The EPMA results also showed that it was greatly difficult to completely remove As from the iron-enriched phase since small amount of As was also found to be evenly distributed in the Fe-enriched phase at 1623 K.

Industrial Application

The current results showed that volatilization of all the volatile matter from the hematite ore depends on the chemical bonds holding the volatile matter in the ore and also that

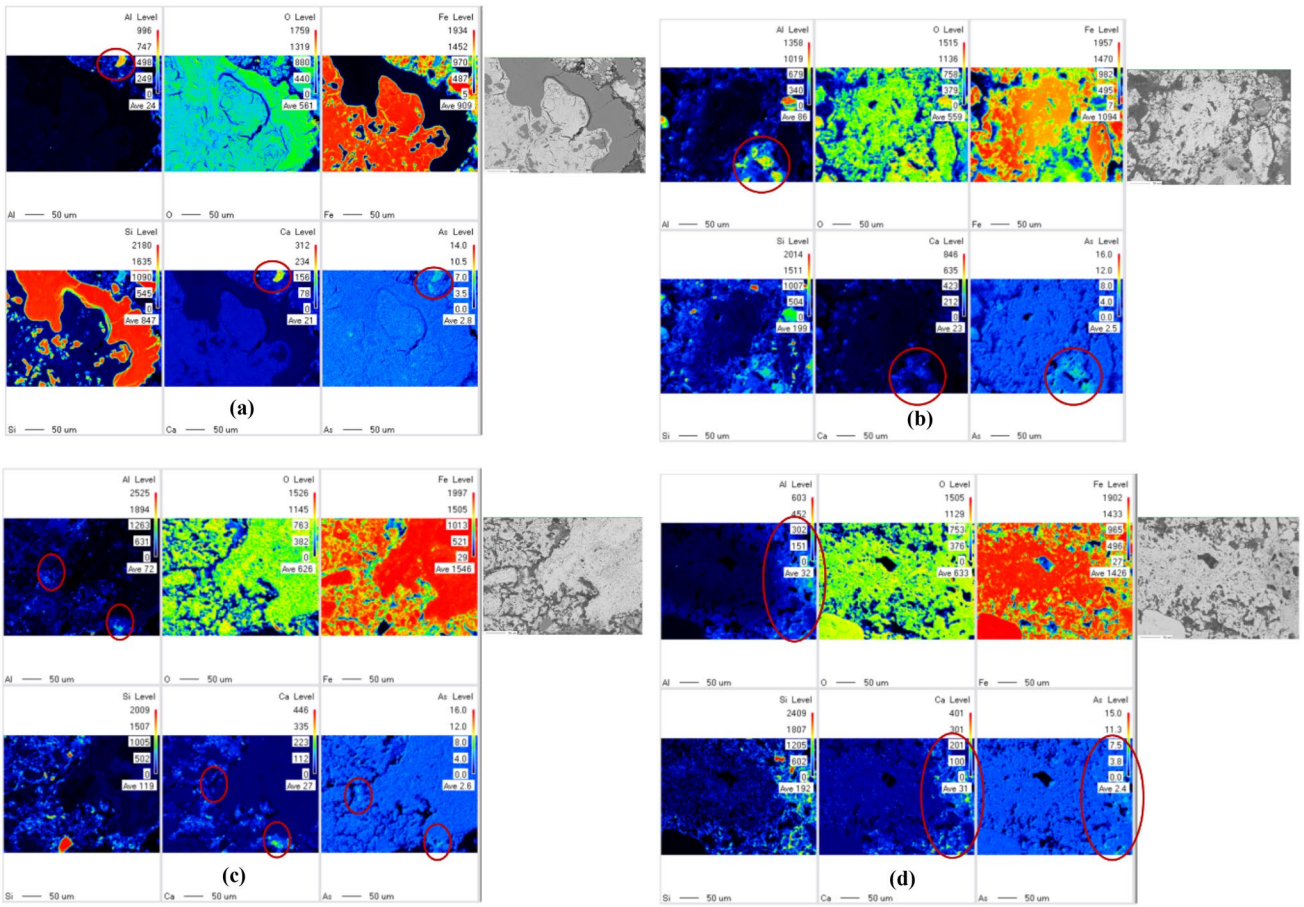


Fig. 7 Elemental mapping of the pellet non-isothermally heated to: **a** 1373 K, **b** 1473 K, **c** 1573 K, and **d** 1623 K

$2CaO{\cdot}As_2O_5(s)$, $3CaO{\cdot}2As_2O_5(s)$, and $AlAsO_4(s)$ were the most stable compounds in the pellet even after heating around 1623 K. These results were in good agreement with the findings from other previous researches [4, 11]. The presence of $CaO(s)$ in sinter has potential of increasing the remaining amount of As inside the sinter by forming the stable $2CaO{\cdot}As_2O_5(s)$.

These results only provide the basic understanding of the behavior of As during non-isothermal heating in an Ar atmosphere. In actual sintering process of iron ore, $CaO(s)$ is intentionally added to produce fluxed and semi-fluxed sinters in a different gaseous atmosphere; more research should be done in reducing and oxidizing conditions to fully understand arsenic volatilization during sintering. Production of acidic sinters should also be investigated since lower amount of As might be trapped inside the sinter in the form of $2CaO{\cdot}As_2O_5(s)$ or $3CaO{\cdot}As_2O_5(s)$.

In other industries of, e.g., gold production where numerous arsenical ores are used, the volatilized As from the off-gas is trapped in the form of an oxide, $As_2O_3(s)$ and stored in bags to prevent environmental pollution [11]. The use of $CaO(s)$ or $Al_2O_3(s)$ to hold As from the off-gas in the form of $2CaO{\cdot}As_2O_5(s)$, $3CaO{\cdot}As_2O_5(s)$, or $AlAsO_4(s)$ should be investigated since these arsenates can thermodynamically be formed and also appears to be stable even at 1623 K. In addition, the calcium arsenate [$3CaO{\cdot}As_2O_5(s)$] has low solubility in water [7].

Conclusions

The volatilization behavior of arsenic from a hematite ore was investigated through the non-isothermal heating of the hematite pellets in argon atmosphere at a temperature range of 298–1623 K employing the TG-DSC and vertical tube furnace. The results obtained were as follows:

(1) Volatilization of As and all other volatile components in the ore increased with increase in temperature, and the volatilization rates depended on the chemical bonds holding the volatile materials in the ore.
(2) Volatilization of As was strongly affected by the interaction with other metallic components in the ore especially with CaO and Al_2O_3. These interactions with different metallic components in the ore limited the complete escape of As from the pellet during the non-isothermal heating process.
(3) $2CaO{\cdot}As_2O_5(s)$, $3CaO{\cdot}As_2O_5(s)$, and $AlAsO_4(s)$ were found to be the most stable arsenic-containing phase and prevented the complete escape of As even at high temperature of 1623 K. Formation of the $2CaO{\cdot}As_2O_5(s)$ or $3CaO{\cdot}As_2O_5(s)$ might be used in developing technologies for As pollution prevention by using $CaO(s)$ to trap gaseous arsenic compounds in the off-gas; further research needs to be carried out in this area.
(4) Similar investigation using reagent grade FeAsS and As_2O_5 in argon and other gaseous atmospheres should be done in order to fully understand As volatilization phenomena.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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