

Resource recovery of founding waste containing transition elements: Conversion into hydrogen sulfide sorbent

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Abstract

The hydrogen sulfide sorptive property of founding dust exhausted from a cupola furnace was investigated at room temperature by X-ray diffraction, transmission electron microscopy, measurement of adsorptive capacity, etc. Consequently, it was found that this property was induced by the spinel-type nanocrystals composed of transition elements in the dust. Furthermore, characterization revealed that the H₂S sorptive capacity of the dust was enhanced by NaOH treatments to extract the spinel-type nanocrystals from amorphous SiO₂ matrix. In addition, it was found that the H₂S sorptive capacity was correlated with Mn content in the spinel-type nanocrystals.

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1. Introduction

Resource recovery technology of solid waste is one of the important subjects for ensuring sustainable development. Therefore, there have been many recent studies on resource recovery of waste. For example, wastes containing Si and Al, such as waste incineration fly ash, coal fly ash, paper sludge, etc., have been proposed to be converted into tobermorite (calcium silicate hydrate) and zeolitic compounds,^{1–9} and used as raw materials for cement.^{10,11} Preparations of active carbon from waste newspaper,^{12,13} tobermorite from chaff¹⁴ and so on have been investigated. There are many areas which have fallen behind in resource recovery technology.

A lot of casts, including those used to make engine blocks, are used in cars, which are indispensable to our life as a means of transportation. Nearly three million tons of casting waste, including one million and some hundred thousand tons of waste casting sand, are discharged from foundries each year by the production of casts. Some of the waste is effectively utilized for construction materials. However, much of the waste has yet to be utilized though it contains useful elements. For

example, although effective use of the waste called cupola dust, which is formed by the solidification of metal vapor generated from a cupola furnace for melting various kinds of scrap metals, has been examined, it is yet to be realized. Thus, as some hundreds of thousand of tons of the cupola dust are landfilled each year in Japan, immediate countermeasures are desired for environmental conservation.

We have investigated processes to convert the cupola dust into useful environmental cleanup materials, such as a deodorizing agent or a substance to remove harmful ions, noting that it contains useful transition elements. Consequently, the cupola dust was discovered to have removal abilities for poisonous gases such as hydrogen sulfide, ammonia, sulfur dioxide, nitrogen dioxide, etc.¹⁵ The cupola dust especially exhibited a good sorptive property for hydrogen sulfide (H₂S) gas. In this paper, we discuss the H₂S sorptive property of the cupola dust in terms of its structure and composition in order to convert into H₂S sorbent.

2. Experimental

Two kinds of cupola dusts, Dusts-1 and -2, were collected from the bag filter in the cooling system interconnected to

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cupolas in Aisin Takaoka Co. Ltd. (Toyota, Japan). Dusts-1 and -2 are discharged from production processes of grey cast iron and ductile cast iron, respectively. Both the cupola dusts were employed in the experiments.

The chemical compositions of the dusts were analyzed by X-ray fluorescence technique (XRF; RIX3000, Rigaku, Japan). The dusts were characterized by powder X-ray diffraction (XRD; RINT2100/PC, Rigaku, Japan) with monochromated Cu K α radiation and scanning electron microscopy (SEM; JSM-6300F, JEOL, Japan). Furthermore, microstructures of the dusts were examined by transmission electron microscopy (TEM; HF-2000, Hitachi, Japan) operated at 200 kV. The chemical compositions of the microstructure were analyzed by energy dispersive X-ray fluorescence technique (EDX; Sigma, KeveX (Noran), U.S.A.).

The H₂S sorptive properties of the dusts were examined by the gravimetric method, using a device with a quartz spring balance in a glass tube connected to a vacuum line. Each dust was dried at 303 K under vacuum lower than 5 Pa in the glass tube, and weighed. Then, water vapor was fed into the glass tube because sorption does not occur in dry circumstances. The relative pressure (P/P_0 ; P is equilibrium pressure and P_0 saturation pressure) was controlled at about $P/P_0 = 0.6$, which corresponds with the mean humidity of the air. The wet dust was weighed after reaching equilibrium. Then, pure H₂S gas was fed into the glass tube up to 20 kPa. The weight of H₂S sorbed on the wet dust was measured after 24 h, and the H₂S sorptive capacity per 1.0 g of the dry dust was evaluated.

The dust was hydrothermally treated in the presence of 0.5–5 M (mol dm⁻³) NaOH (Kanto Kagaku) aqueous solution with solid/liquid ratios of 1/30–1/4. The treatments were performed at 353–398 K for 4.5–41 h in a Teflon-lined autoclave under an autogeneous pressure with continuous stirring. The products were filtered and repeatedly washed with deionized water after the treatment. The resulting materials were dried at 333 K for 24 h and ground for further analyses, i.e. XRD, TEM and measurement of H₂S sorptive capacity.

3. Results and discussion

Prior to the experiments, it was confirmed that no distinct variations in the chemical compositions and crystalline phases, which are important factors in the resource recovery processes, had been detected in the long-term. Fig. 1(a) and (b) exhibit the XRD patterns of Dusts-1 and -2, respectively. The main crystalline phase in Dust-1 was identified as a spinel-type compound ($M^{\text{II}}M^{\text{III}}_2\text{O}_4$; M = metal ion), accompanied by small amounts of quartz and Zn₂SiO₄, while those in Dust-2 were identified as a spinel-type compound and ZnO, accompanied by small amounts of quartz, Zn₂SiO₄ and Fe₂O₃. The chemical compositions, as listed in Table 1, revealed that both the dusts included Fe and Zn as the main transition elements, and much Mn next to them. As a result, the spinel-type compound was supposed to be composed of Fe, Zn and Mn, i.e. (Zn, Fe, Mn)₃O₄.

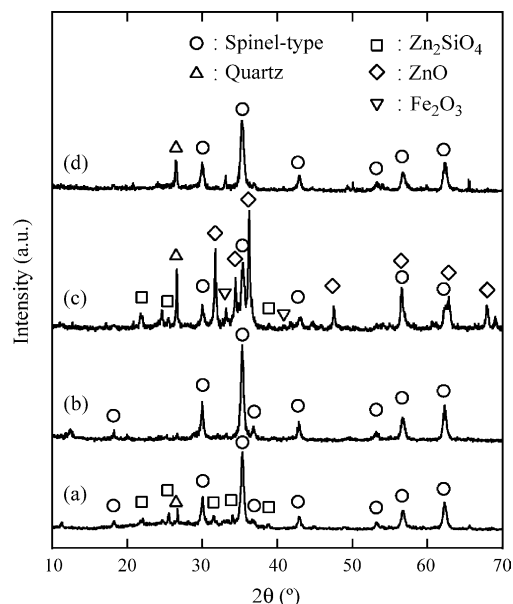


Fig. 1. XRD patterns of Dusts-1 and -2 before and after NaOH treatments. (a) Untreated Dust-1; (b) 5 M NaOH-treated Dust-1; (c) untreated Dust-2; and (d) 5 M NaOH-treated Dust-2.

SEM showed that Dusts-1 and -2 were fine spherical-shaped particles with a mean diameter of ca. 200 nm. TEM-EDX observations were then made in order to clarify the grain structure. Fig. 2 illustrates the TEM images of Dusts-1 and -2. TEM revealed that opaque particles 10–50 nm in dimension were dispersed within a translucent spherical-shaped matrix. In addition, some non-spherical-shaped particles, which adhered to the spherical-shaped particles, were observed in Dust-2. The structure and chemical composition of the translucent, opaque and non-spherical-shaped parts were examined by the electron diffraction and EDX, referring to the XRD patterns. Consequently, the translucent part was found to be amorphous SiO₂, while most of the opaque

Table 1
Chemical compositions of cupola dust

Component	Content (mass%)	
	Dust-1	Dust-2
O	39.5	37.8
Mg	0.6	0.5
Al	2.2	1.2
Si	15.5	7.5
P	0.1	0.1
S	0.3	0.2
Cl	0.9	0.5
K	1.3	0.9
Ca	4.1	1.5
Ti	–	0.1
Mn	7.8	2.1
Fe	11.8	13.2
Zn	15.3	34.1
Sn	0.1	0.1
Pb	0.4	0.2

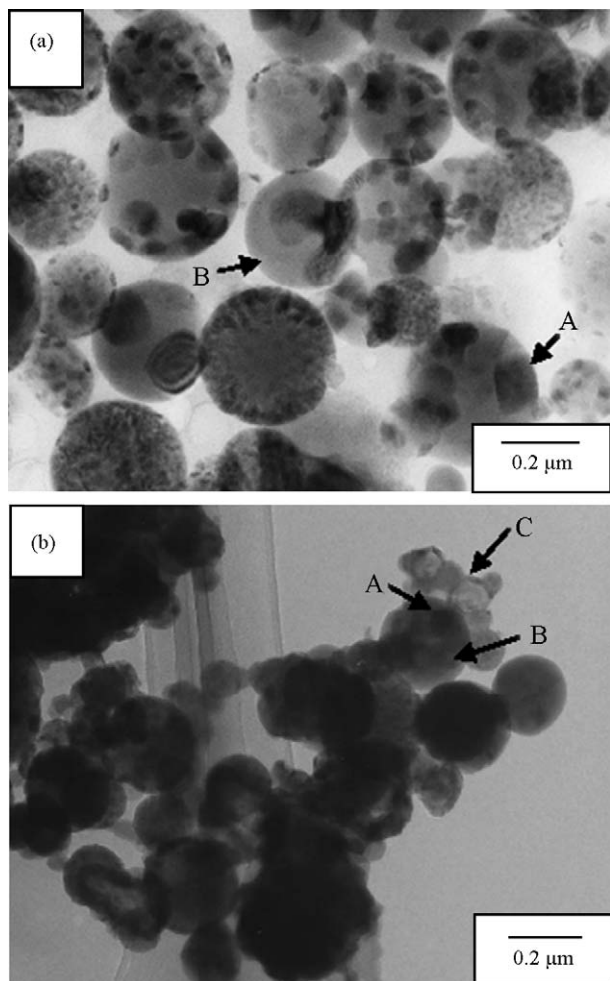


Fig. 2. TEM images of (a) Dust-1 and (b) Dust-2. A, spinel-type nanocrystal; B, amorphous SiO₂ matrix; and C, ZnO particle.

parts were identified as spinel-type nanocrystals, though a small amount of Zn₂SiO₄ was observed. The non-spherical-shaped part was identified as ZnO.

The spinel-type nanocrystals were assayed by EDX in order to evaluate their chemical compositions. From the results, the atomic ratios of Fe, Zn, Mn and O in Dust-1 were estimated to be 18.3–20.1, 12.3–12.8, 9.2–10.0 and 58.0–59.7%, respectively. The ratios of total metal and O were about 60 and 40%, respectively, which are close to those in the ideal spinel-type compound (M^{II}M^{III}₂O₄). Then, which sites Fe, Zn and Mn occupied was examined, assuming that the spinel-type nanocrystals are stoichiometric compounds. It was supposed that Fe and Zn preferentially occupied M^{III} and M^{II} sites, respectively, whereas Mn occupied both the sites, referring to the spinel-type compounds such as ZnFe₂O₄, MnFe₂O₄ and ZnMn₂O₄.¹⁶ The analyzed atomic ratios of Fe and Zn were rather low, compared with the ideal atomic ratios of the M^{III} and M^{II} sites, i.e. 28.6 and 14.3% for the M^{III} and M^{II} sites, respectively. The spinel-type nanocrystals in Dust-1 were, therefore, identified as mainly a substitutional solid solution of ZnFe₂O₄, whose M^{II} and M^{III} sites are partly

occupied by Mn, that is, (Mn_xZn_{1-x})(Mn_yFe_{1-y})₂O₄ solid solutions.

On the other hand, the atomic ratios of Fe, Zn, Mn and O in Dust-2 were estimated to be 19.9–21.3, 14.1–14.8, 3.6–3.8 and 60.2–62.4%, respectively. The site occupancies of Fe, Zn and Mn were examined in a similar manner, as the ratios of total metal and O were close to those in the ideal spinel-type compound. Consequently, the spinel-type nanocrystals in Dust-2 were identified as mainly a substitutional solid solution of ZnFe₂O₄, whose M^{III} site is partly occupied by Mn, that is, Zn(Mn_yFe_{1-y})₂O₄ solid solutions because the atomic ratio of Zn was close to the ideal atomic ratio of the M^{II} site, i.e. 14.3%.

The H₂S sorptive capacities of Dusts-1 and -2 were estimated to be about 0.08 and 0.04 g g⁻¹, respectively, by the gravimetric method. The spinel-type nanocrystals in both the dusts were considered to play an important role in sorbing H₂S gas, referring to the studies on H₂S sorptions of ZnFe₂O₄ and CuMn₂O₄ at elevated temperature.^{17–20} The H₂S sorptive capacities of Dusts-1 and -2 were, however, considerably low, compared with ZnFe₂O₄ (Johnson Matthey, London, U.K.) and an Fe-based sorbent (Nissan Girdner Catalyst, Tokyo, Japan) on the market, whose H₂S sorptive capacities were measured to be 0.29 and 0.27 g g⁻¹ at room temperature, respectively. This was elucidated to be due to hardly any spinel-type nanocrystals in the inside of the SiO₂ matrix being available for H₂S sorption.

The dusts were then hydrothermally treated in the presence of NaOH solution to dissolve the amorphous SiO₂ matrix and extract the spinel-type nanocrystals. First, both the dusts were treated in the presence of 0.5–5 M NaOH solutions with a solid/liquid ratio of 1/30 at 373 K for 24 h. XRD exhibited that the crystalline phases, except of the spinel-type compound, decreased with increasing NaOH concentration, and the spinel-type compound remained as a dominant phase after the 5 M NaOH treatment, as shown in Fig. 1(b) and (d). The analytical results of the 5 M NaOH-treated dusts by an XRF technique revealed that the atomic ratios of Fe, Zn and Mn got closer to those in the spinel-type nanocrystals analyzed by TEM-EDX. The TEM image of the 5 M NaOH-treated Dust-1 is shown in Fig. 3, showing that most of the spinel-type nanocrystals were extracted by the destruction of the spherical-shaped matrixes, and a small amount of amorphous SiO₂ stayed among the spinel-type nanocrystals as binders.

The effect of NaOH treatment on the H₂S sorptive capacity was examined. Fig. 4 presents the H₂S sorptive capacities of Dusts-1 and -2 as a function of NaOH concentration used in the treatments. The H₂S sorptive capacities of both the NaOH-treated dusts increased with increasing NaOH concentration, and reached about three times as high as those of the untreated dusts when 5 M NaOH was used. These results indicate that the H₂S sorptive capacity is primary induced by the spinel-type nanocrystals, such as (Mn_xZn_{1-x})(Mn_yFe_{1-y})₂O₄ and Zn(Mn_yFe_{1-y})₂O₄ solid solutions in both the dusts. In particular, the H₂S sorptive

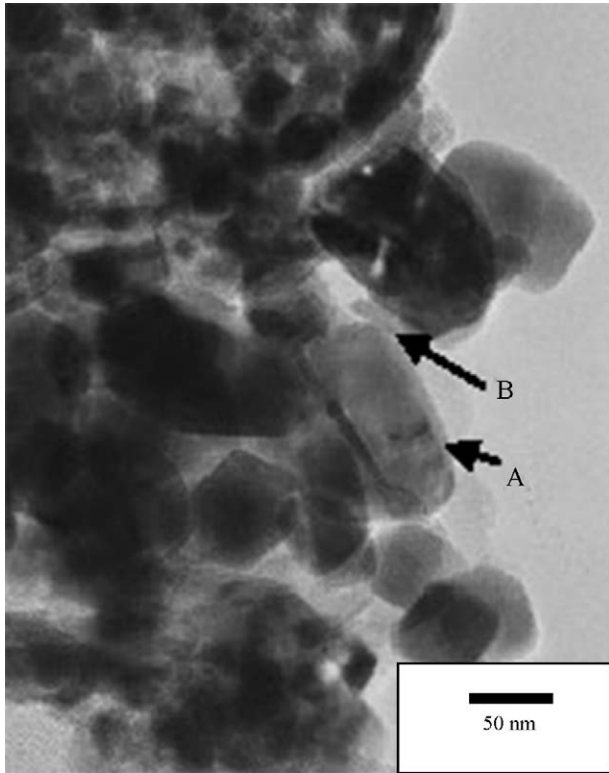


Fig. 3. TEM image of Dust-1 after 5 M NaOH treatment. A, spinel-type nanocrystal and B, amorphous SiO_2 .

capacity of Dust-1 was drastically enhanced by the NaOH treatments, and that of the 5 M NaOH-treated Dust-1 was found to compare with those of ZnFe_2O_4 and an Fe-based sorbent on the market.

Furthermore, Dust-1 was treated with 5 M NaOH solutions under such reaction conditions that solid/liquid ratios, reaction temperatures and reaction times were different. The H_2S sorptive capacities of the resulting materials were measured, and plotted versus each transition element content in the treated Dust-1, as shown in Fig. 5. The plots revealed that there is a high correlation between the H_2S sorptive capacity and the Mn content. Namely, H_2S sorptive capacity was found

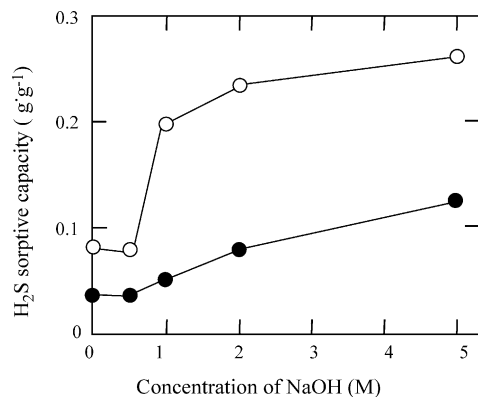


Fig. 4. H_2S sorptive capacities of Dust-1 (open circle) and Dust-2 (filled circle) as a function of NaOH concentration used in the treatments.

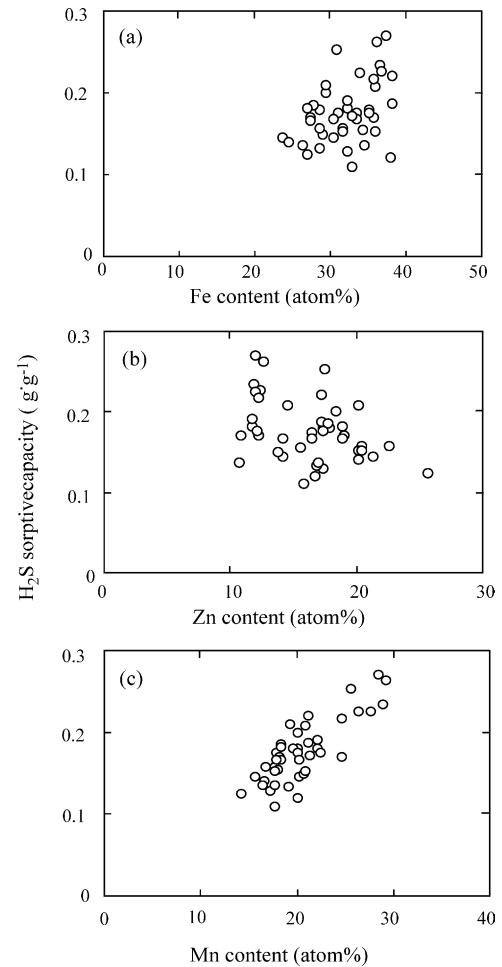


Fig. 5. Plots of H_2S sorptive capacities vs. (a) Fe; (b) Zn; and (c) Mn contents in NaOH-treated Dust-1 under various hydrothermal conditions.

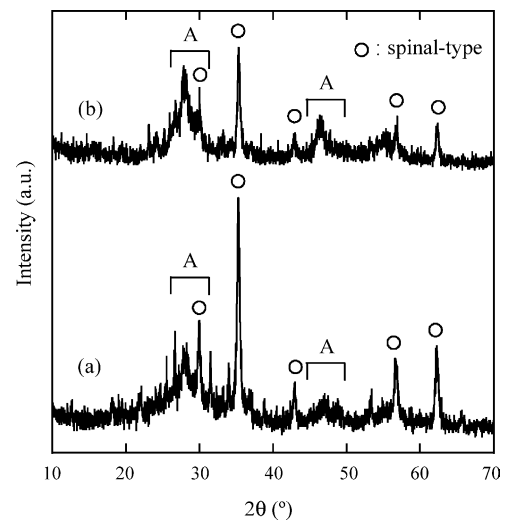


Fig. 6. XRD patterns of (a) untreated Dust-1 and (b) 5 M NaOH-treated Dust-1 after contacting with H_2S gas. Open circle, spinel-type compound and A, sulfide compounds such as FeS , ZnS and MnS .

to be promoted by increasing Mn content. This is consistent with the fact that the spinel-type nanocrystals with high Mn content in Dust-1 have higher H₂S sorptive capacities than those with low Mn content in Dust-2.

Fig. 6 shows XRD patterns of the untreated Dust-1 and 5 M NaOH-treated Dust-1 after contacting with H₂S gas. New broad peaks in the ranges of $2\theta = 25\text{--}30^\circ$ and $45\text{--}50^\circ$, assigned to sulfide compounds such as FeS, ZnS and MnS, appeared. The XRD intensities of the broad peaks increased with increasing NaOH concentration used in the treatments, and those based on the spinel-type nanocrystals decreased. A similar phenomenon was observed in Dust-2. From the results, H₂S gas was found to be removed by chemical reactions with the spinel-type nanocrystals in both the dusts.

4. Conclusion

The H₂S sorptive properties of two kinds of founding dusts, Dusts-1 and -2, exhausted from cupola furnaces for the productions of grey and ductile cast irons, respectively, have been investigated at room temperature, aiming at resource recovery. From the results, the following were found. Dust-1 was fine spherical-shaped particles consisting of mainly amorphous SiO₂ with some dispersed spinel-type nanocrystals, such as (Mn_xZn_{1-x})(Mn_yFe_{1-y})₂O₄ solid solutions, while Dust-2 was a mixture of fine spherical-shaped particles consisting of mainly amorphous SiO₂ with some dispersed spinel-type nanocrystals, such as Zn(Mn_yFe_{1-y})₂O₄ solid solutions, and fine non-spherical-shaped ZnO particles. Both the spinel-type nanocrystals could remove H₂S gas through chemical reactions, and the H₂S sorptive capacity was enhanced by the NaOH treatments to extract the spinel-type nanocrystals. Furthermore, the H₂S sorptive capacity increased with increasing Mn content in the spinel-type nanocrystals. The 5 M NaOH-treated Dust-1 could be utilized as an H₂S sorbent at room temperature because its H₂S sorptive capacity is comparable to those of other H₂S sorbents on the market.

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