Application of Microwave Technique for Dehydration of Sludge Generated in a Stainless Steel Plant

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In ironmaking and steelmaking processes, dehydration technology is often recognized to be a key process for the successful operation. That is not an exception in recycling process of valuable elements such as Fe, Ni, Cr and so on by reducing the wasted materials including dust, scales and sludge, generated in each steel works. This investigation basically focused on the availability of microwave technique for dehydration stage of sludge generated in a stainless steel mill. Actually sludge is well-known as a wasted resource difficult to be dehydrated. Unless dehydration of such resource is successful, some problems with slow heating and/or burst of briquettes may arise.

In this study, prior to the industrial studies, dehydration experiments of goethite were performed. The results showed that the microwave treatment could heat up the specimen directly from inside of specimen while being heated from the outside by the electric furnace. Thus the dehydration ratio resulted higher in the microwave irradiation, indicating the benefit of the microwave treatment.

Thereafter the microwave technique was tried for dehydration of industrial sludge. Consequently, the effectiveness of microwave treatment was confirmed because 34 mass% weight-loss after the microwave treatment corresponded to the complete dehydration while 7 mass% weight-loss after heating in a conventional electric furnace. If application to industrial practice is realized, it is expected that the problems brought by the conventional way will be hopefully solved to prevent burst of agglomerations.

KEY WORDS: microwave; sludge; recycling; dehydration; goethite; briquette.

1. Introduction

The tasks to reduce manufacturing costs have been always carried on by ironmakers and steelmakers. In the costs, most recently, the ratio of raw materials for products to overhead costs such as personnel expenses are quite rapidly getting higher. Consequently the prices eventually depend on how to choose raw materials as low as possible in cost. Iron ore price increases and subsequently affects industries such as automobiles and electric products.

Along with the iron ore problem, the prices of Ni, Cr, Mn and Mo for specialty steels have been also seriously increasing as well as a significant extent of changing in price at a time. Therefore, especially, steelmakers have made a lot of tasks to select how to blend raw materials to achieve the lowest cost.

Under this situation, wasted materials generated internally in the steel plants are significantly focused on for recycling of valuable resources, which include dust from steelmaking shops, sludge and scale generated from annealing and pickling lines in hot and cold rolling shops and so forth. Those resources contain a substantial amount of valuable elements such as Ni, Cr, Mn and Fe in the case of stainless steel plants. A process flow as an example is schematically illustrated in Fig. 1 basically modifying that for the production of ferroalloys. Resources, one of which wet sludge is preliminarily dried, are firstly blended adding adequate amount of water to give enough strength for subsequent briquettes shaped by twin-roll equipment. They are thereafter roasted aiming at drying, preheating and semi-reduction. Finally, those briquettes are charged into the submerged type electric furnace with cokes for reduction and heating to obtain metal consisting of Fe–Cr–

![Fig. 1. Schematic illustration of flow chart for recycling. Underlined stages are candidates for the replacement to microwave equipments.](image-url)
Ni–Mn separating from slag. In this field, basic studies have been conducted to thermodynamically clarify the mechanism to reduce those valuable elements from sludge by way of carbo-thermal reduction. Regarding a safety issue, Naruse pointed out that explosion may occur in the case of SiMn or FeMn production because of abrupt CO gas evolution. It is also postulated that burst in the furnace by remained water may take place unless dehydration of sludge that is very wet and/or drying of briquettes when roasting is enough.

This study basically focuses on the dehydration operation of stainless steel sludge known to be difficult to remove water applying a microwave process. Besides, it is compared with the conventional operations such as a rotary kiln or burned dryer that are basically heated from the surface of briquettes by burner flames.

Namely, radiation to the surface of the briquettes is the initial heat source after which temperature gradually increases toward inside mainly by conduction. If the initial heat input by radiation is too much, partial melting and subsequent sintering may occur resulting in the obstruction of mass transfer from the inside toward the surface, which of course involves water removal. On the other hand, microwave method is expected to enable directly heat up the whole part of the briquettes under the conditions where conductive elements exist. According to the review paper by Bai, in fact, beneficial effect of microwave to dry agglomerates of iron ore for a blast furnace has been proved. They also pointed out the problems of the conventional way in that the dry speed is slow and the green ball is easily burst due to the same mechanism stated above.

Besides, there are several reports on attempts of microwave treatments of sewage sludge and some industrial sludge produced in acid extraction or etching of circuit boards, however, there are much less attempts performed to apply microwave heating for the sludge in iron and steel-making processes.

Prior to the practical recycling materials, dehydration experiments have been undertaken employing simple mineral of goethite FeO(OH). Nambu has studied the changing behavior from natural goethite to hematite with goethite put in a Pt crucible heated by a small electric furnace. Their focus was on the crystallization behavior and no industrial application was stated. Nishifuji has developed monitoring system of dehydration of iron ore because many ironmakers are afraid that imported ores with lower grades having more combined water increases in the near future. Typical mineral of such is mentioned as α-goethite in their report. Thus one can easily understand that the more effective dehydration process than conventional way is becoming more important not only in recycling process but iron ore pre-treatment also.

The final goal of this study is to discuss the possibility to technically replace dehydration operation to microwave method instead of pre-treatment heating for sludge by the burner in Fig. 1. The roasting stage in Fig. 1 might be replaced by microwave equipments, too. In the present work, the former issue will be discussed while the latter will be summarized next.

2. Experimental Details

2.1. Goethite

Powder specimen of FeO(OH) (Nakaraitesuku Co., Ltd.) was mixed with graphite (Kojundo Chemical Laboratory Co., Ltd.: 5 µm in average particle size) powder for heat source. The molar ratio of FeO(OH): graphite was adjusted to 1:2. The mixture weighed as 6.2 g, charged into quartz crucible as shown in Fig. 2, was heated up to 200, 300, 350, 400, 500 and 600°C and then held for 10 min flowing nitrogen gas with 500 mL/min. Heating ratio was chosen as 50, 100 or 150°C/min to determine the effect on weight loss. Temperatures were measured by a K-type sheath thermocouple. As for a microwave apparatus shown in Fig. 3, multimode applicator (Shikoku Keisoku, max power 0.67 kW, wave-frequency 2.45 GHz) was used. The detail of description about the apparatus has been documented elsewhere. Concurrently weight loss was measured with the electronic balance (AND GX-6100/A&D Co., Ltd.) positioned above the microwave lifting the specimen contained in the crucible with the thin cords as seen in Fig. 3. In order to avoid the obstructive effect by thermocouple on the weighing, its tip was positioned 15 mm above the bottom of the silica tubing as seen in Fig. 2.

For comparison, the same set-up as in Fig. 2 was positioned in an electric furnace and heated up to the aimed temperatures. In this case, it was impossible to install thermal balance for simultaneous weight measurement. Hence the specimen together with the crucible was weighed after taking it out and cooled down. In both experiments, XRD (Rad-C, Rigaku) analysis was carried out to identify the consisting phases of the specimens to examine how goethite changes.

2.2. Sludge

Industrial sludge, whose appearance is shown in Fig. 4, has been originally very wet with approximately 50 mass%
water followed by dried by burner shown in Fig. 1 at about 400 to 500°C for 10 min. This specimen was examined with DTA and TG (Seiko Instruments Inc. Exstar6000, TG/DTA6300) in order to determine its thermal response from room temperature to high temperature (∼1200°C). The condition was that initial sample weight was 25 mg and blank alumina pan was used for reference substance. The heating rate was adjusted as 10°C/min.

Then, the specimen was prepared in the same manner as in Fig. 2 to understand dehydration behavior. The specimen of 15 g, in which graphite was mixed at the same ratio as in the case of goethite, was heated to 100, 120 and 150°C with heating rate of 50°C/min and then held for 30 min. In spite of the above drying treatment, 20 to 30 mass% of water usually remains. This specimen had water of 30 mass% at the beginning. A typical composition is provided in Table 1 (no water content listed). Wasted pickled solutions are neutralized by CaO so that Ca is enriched. Preliminary XRD analysis showed no apparent peaks implying that sludge should be amorphous.

The other conditions regarding the microwave were the same as in the goethite experiments. As well, experiments were carried out being heated by an electric furnace for comparison.

3. Results and Discussion

3.1. Goethite

3.1.1. Microwave

Figure 5 shows the effect of holding temperatures on phase fractions detected by XRD analysis. Every experiment was conducted with the fixed heating rate of 100°C/min. Obviously the ratio of hematite increases with increasing temperature. It is noted here that because the structure of Fe₂O₃ is quite similar to that of Fe₃O₄, it is difficult to identify the existence of Fe₃O₄, precisely. However, the peak height of graphite detected by XRD did not differ at every temperature so that reduction of FeO(OH) by C to form Fe₂O₃ must not have occurred very much. Hence, the detected substance was considered as only Fe₂O₃ formed as a result of dehydration. Figure 6 shows the rates of weight loss at various holding temperature. A tendency can be seen that dehydration rate is becoming drastically faster from 300 to 400°C. This implies that dehydration reaction is most vigorous at this temperature range. This result well agrees with that by Nambu demonstrating that dehydration temperature is around 350°C experimented by DTA.

Figures 7(a), 7(b) and 7(c) show the effect of heating rate of 50, 100 or 150°C/min, respectively, on the dehydration starting temperature, initial weight loss rate when heated up and weight loss rate at the steady-state at 350°C. The following facts are obviously understood;

a) Dehydration starts at around 200°C in every case.

b) Initial weight loss rate when heated up increases with increasing heating rate.

c) Weight loss rate at the steady-state after attaining 350°C is almost constant in every case.

Here, equilibrium of dehydration is considered. FeO(OH) decomposes according to the following reaction.17)

\[
2\text{FeO(OH)}(s) \rightarrow \text{Fe}_2\text{O}_3(s) + \text{H}_2\text{O}(g) \uparrow, \quad \Delta G^\circ(0 \, T) = 192°C
\]

The heat of formation for FeO(OH) is as follows.18)

\[
\Delta H^\circ = -558.1 \text{ (kJ·mol}^{-1}) \quad \text{(2)}
\]

With the above value of (2), one can calculate heat of reaction at 298 K as below.

\[
\Delta H^\circ_{298} = 26.545 \text{ (kJ·mol}^{-1}) \quad \text{(3)}
\]

This shows that dehydration of FeO(OH) is endothermic reaction.

The result of a) is well explained by the equilibrium calculation by Eq. (1) where it begins at 192°C. The reason of
result b) is thought to be attributed by the more heat input per unit time with increasing heating rate to compensate the endothermic. That is why initial weight loss rate increases with increasing heating rate. Namely, the dehydration rate is determined being controlled by heat supply into the specimen. Concerning c), it should be caused by gradual steady-state reaction at constant temperature of 350°C.

To better understand the above phenomena, microwave power was kept as 37 W with the sample being heated for 10 min. As can be seen in Fig. 8, heating rate apparently decreases at 200°C of equilibrium decomposition temperature. This implies the following mechanism. Before dehydration the power is exhausted only for the heating owing to graphite. However, after that the power is exhausted for both heating materials and dehydration whose reaction is endothermic.

3.1.2. Electric Furnace

In order for microwave effect to be more clearly shown, heating by an electric furnace was performed. At first, weight change was compared to the microwave. The result showed that, by the microwave, the weight decreased from 5.0470 to 4.6008 g, while 5.2578 to 5.1281 g by the electric furnace, proving the more beneficial effect of the microwave.

Figures 9(a) and 9(b) show the appearance of whole and cross-sectional views after the microwave experiment, respectively. Obviously, the color of center part changed from original goethite of brown to dark red of hematite, as identified by XRD. Because microwave can heat the specimen internally and heat loss occurs from the outer region, the temperature becomes higher in the internal area.

On the other hand, Figs. 10(a) and 10(b) show the appearance of whole and cross-sectional views after electric furnace experiment, respectively. From (b), dark red region exists along the crucible while inside is remained as original color.

In the electric furnace, specimens are heated by conduction or radiation from the heater, so naturally the specimen is heated from the outer region, resulting in the higher temperature in the outer region. The temperature distributions formed are opposite each other.

3.2. Sludge

Figures 11(a) and 11(b) show the results of DTA and TG analysis of sludge, respectively. The DTA data shows endothermic behavior at around 100°C corresponding to the
boiling point of water. At this temperature, significant weight loss is obvious in the TG curve. This is the vaporization of the adhered water and is different from the decomposition of the combined water of goethite case.

In the microwave experiment heated up to 150°C provided in Fig. 12, weight loss caused by dehydration started at 120°C below which no change is seen. It should be notified that 4 g in weight (initial weight 15 g) was lost during the first 9 min. This corresponds to 80% of total loss during the holding time of 33 min implying that dehydration very rapidly proceeds. Another notice is that temperature drop along with weight gain simultaneously took place at 285 s pointed by an arrow in Fig. 12. This extraordinary behavior is attributed to a lot of dews precipitated at the ceiling of the apparatus resulted from the active dehydration as shown in Fig. 13. The extraordinary behavior was considered to be brought by dropping these dews into the tubing holding thermocouple. This phenomenon was not observed in the case of goethite experiments. Therefore, dehydration of sludge is considered to be even more vigorous.

To understand why dehydration started at 120°C which is slightly above 100°C corresponding to the boiling point of water, another experiments were carried out with holding at 100 and 120°C as shown in Figures 14(a) and 14(b), respectively. The experiment of 100°C (a) shows that weight loss linearly and very gradually proceeds and that eventual weight loss is as small as 1 g. On the other hand, faster dehydration is apparent when the specimen was held at 120°C and eventual weight loss attained about 4 g. This result has proved that microwave power for 120°C is necessary for effective dehydration and that this gives us a way how one controls in industry.

Table 2 summarizes the results obtained from the sludge experiments comparing with that of electric furnace. Effectiveness of the microwave treatment is obvious. 34 mass% weight-loss corresponds to the complete dehydration because the specimen initially contained 30 mass% water even after drying by the burner. Lower effectiveness by the electric furnace heating is attributed to the same reason as with
the goethite experiments.

The microwave method has benefit in that water can be directly induced to be boiled. Another benefit is that the core of a specimen starts to be heated bringing higher vapor pressure inside. The higher pressure effectively pushes out water vapor toward outside enhancing dehydration. With the electric furnace, on the other hand, a specimen is heated from the surface where dry starts. Once the surface is dried, contacts between particles become scarce because water has a roll to keep their contacts. Then thermal conduction of the outside gets worse and therefore it leads to difficulty in heat supply toward the inside. Thus microwave has a unique characteristic which the directions are the same in heat and mass transfers while the corresponding directions are opposite with the conventional electric furnace heating.

In this way, the microwave method has been proved to enable dehydration effectively. Indeed, technologically speaking, microwave is competitive with the conventional heating equipments. As mentioned earlier, if application to industrial practice is realized, the problems brought by the conventional way can be solved to prevent burst of agglomerations. For commercialization, however, capital unit of electric consumption of practical sized microwave has to be accounted for. Next study will be stepped up to practical level using industrial briquettes.

4. Conclusions

Dehydration experiments of goethite were performed to pursue the availability of microwave technique. The following results were obtained.

1. Dehydration took place over 200°C which well accords with the thermodynamic calculation. The reaction became more vigorous with increasing holding temperature.

2. The most adequate temperatures for dehydration was found to be ranging between 300 and 400°C.

3. The microwave treatment could heat up the specimen directly from inside while from outside being heated by the electric furnace. Therefore microwave treatment was proved to be more beneficial.

Followed by the goethite experiments, industrial sludge was also treated by the microwave for dehydration to discuss the possibility of practical use comparing with the electric furnace. The followings summarize this investigation.

1. Dehydration took place over 120°C slightly above the boiling point of water (100°C).

2. The extent of dehydration was as vigorous as a number of dews were precipitated inside the microwave apparatus.

3. The effectiveness of microwave treatment has been confirmed by the above results. 34 mass% weight-loss measured by the installed balance corresponded to the complete dehydration.

4. It was cleared that the microwave technology enabled to remove water even more effectively. If application to industrial practice is realized, it is expected that the problems brought by the conventional way will be solved.

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