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Waste Acid Recycling Technology by Slag

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Abstract

In this study, we aim to be separated using a waste acid house recyclable Fe and Ca in the steel making slag, can be reused as raw material for iron making. Specifically, we used the waste hydrochloric acid generated in the pickling line, waste sulfuric acid made in coke chemical plant. In a CaCl₂ solution was selectively dissolving the Ca, and reused as iron source and the residue in hydrochloric acid. The gypsum of reacting with sulfate ions Ca selectively, and recovered as hydroxide Fe in the specific pH range of the particular metal components other than Ca of dissolved and reused as an iron source in the sulfuric acid system.

1. Introduction

Steelmaking slag (hereafter referred to as slag) that occurs in the converters, secondary refining processes, etc. at steelworks contains lime in the form of free lime (hereafter referred to as free CaO). Therefore, it is well-known that when slag is directly used as a material in road construction, civil engineering work, etc., it expands as the free CaO is hydrated. To prevent the expansion of slag, it is common practice to apply aging, wherein the slag is cooled, ground, and left piled up in the open air or reacted with steam to convert the free CaO into Ca(OH)₂. However, the aging process takes approximately one week and requires a significant amount of space within the steelworks.

2. Development of Technologies for Reforming/ Separating Slag and Dust

Even when slag is aged for use as a material in road construction, civil engineering work, etc., the demand for aged slag considerably depends on the prevailing climate of investment in public works as well as on various other economic conditions. Therefore, it is possible that large volumes of slag remain within the steelworks and impede the steel manufacturing operation.

In the past, studies have reported the stabilization of free CaO in slag by treating it with waste acid obtained from the pickling plant of the steelworks. This is a method of slag reformation, whereby the slag containing free CaO is immersed in waste acid (pH = -1-4, temperature = 60°C or higher). In this method, the free CaO is converted into neutral salt, which is then removed or left in the slag. However, heating slag to a temperature of 60°C or higher poses a safety concern and cannot be applied to process large slag volumes.

Another method of reforming slag was also investigated, i.e., carbonation aging, in which granular slag is first pickled and then contacted with a gas containing carbon dioxide or carbonated water in a highly humid atmosphere. With this method, the preliminary pickling of slag facilitates the free CaO in the slag to react with the gas and promotes the carbonation reaction, enabling the manufacture of solid products with sufficient strength. On the other hand, the slag pickling takes more than six hours and the entire process requires a number of large-scale facilities. Ca dissolved in the acid in either of the abovementioned methods is not reused as a raw material in steelmaking.

Although this is not a method for reforming slag, an attempt has been made to recover heavy metals from the dust emitted from a rotary kiln used to obtain limestone clinker or an incinerator by separating the heavy metals from Ca compounds. Further, the heavy metal components of fly ash from a high temperature treatment furnace are recovered in the form of condensates according to the metal type by a series of wet processes. The technology that has been developed for recovering heavy metals separately sorts heavy metal compounds from calcium compounds that are used as raw materials for cement from the dust coming out of the kiln for making clinker for cement.

In the recovery of Pb, Zn, Cu, etc. from the fly ash of an urban garbage incinerator Pb is recovered first by precipitation in an acid (pH \leq 3). Then, a sulfurizing agent (pH \geq 7) is added to recover Zn and Cu in the form of sulfides. In this case, however, Ca is discarded.

To recover Pb, Zn, Fe, Ca, etc. from the dust of a rotary kiln precipitator, a sulfurizing agent (pH = 6.5-8) is first added to recover

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Fig. 1 Separation of steelmaking slag and the ratio of the typical metal oxide

Pb and Zn in the form of sulfides. Then the pH is increased from 8 to 12 to recover Fe and Ca in the form of hydroxides (raw materials for cement). In this case, however, Fe and Ca are not separated (**Fig. 1**).

3. Purpose and Methods of Recycling Ca and Fe Contained in Slag

Apart from the technology for stabilizing the free CaO present in slag by aging, efforts to develop a technology for recycling slag components as raw materials in steelmaking have seldom been made in the past. The purpose of the present study is to separately recover Ca and Fe from slag and reuse them in the steelmaking process.

We developed two recovery methods, one using waste hydrochloric acid $^{\rm 1)}$ and the other using waste sulfuric acid or coke-derived sulfuric acid. $^{\rm 2)}$

In the first method, slag is treated in dilute hydrochloric acid obtained by diluting waste hydrochloric acid (7% to 9%) from the pickling process. Then, Ca in the slag is dissolved in the solution in the form of CaCl₂ (Ca²⁺, 2Cl⁻) in a few minutes, whereas other metallic compounds of Fe, Si, Mg remain undissolved in the dilute hydrochloric acid. Thus, it is possible to easily and economically separate Ca.¹⁾ This technology is widely applicable not only for slag but also for dust, fly ash, waste refractories, etc., which contain Ca and Fe.

When slag is treated in dilute hydrochloric acid solution in a dissolving tank, Ca is ionized in the form of CaCl₂ in the solution, while Fe and other components remain undissolved. The CaCl₂ solution is directly subjected to electrolysis to dissociate it into Cl₂, H₂, and Ca(OH)₂. Alternatively, the CaCl₂ solution is added to NaOH solution to increase its pH stepwise (from acid to alkaline) in order to precipitate Fe(OH)₃ at pH of 3–4, Al(OH)₃ and Cr(OH)₃ at pH of 5–6, Fe(OH)₂ at pH of 8–9, Mn(OH)₂ at pH of 9–10, and Mg(OH)₂ at pH of 9.5–10.5. After separation, the targeted Ca(OH)₂ that remains largely undissolved in the solution is obtained at a pH of 11– 13. The NaCl solution that has been removed from Ca(OH)₂ is subjected to electrolysis to recover NaOH and Cl₂ (in the form of HCl obtained by reaction with H₂), which are then reused in the abovementioned process (**Fig. 2**).

Figure 3 shows the amount of dilute hydrochloric acid required to dissolve slag, the amount of NaOH required to hydrate slag, and the amount of recoverable $Ca(OH)_2$ each per ton of slag. As mentioned above, both hydrochloric acid and NaOH can be recycled via electrolysis.

In the other method, the slag is immersed in a solution obtained by diluting concentrated sulfuric acid obtained from a coke plant to 10%-40%. Then, Ca becomes insoluble CaSO₄, whereas Fe, Al, Cr, Mn, and P are ionized in the sulfuric acid solution. Therefore, CaSO₄ and Fe can be recovered separately (**Fig. 4**). Because P ionized in the sulfuric acid solution has a high value, a method for separating it from sulfuric acid ions has also been developed.

Figure 5 shows the amount of sulfuric acid (20%) required to

1) After dissolving the slag in hydrochloric acid, and $\mbox{Ca}\,\mbox{OH})_2$ recovery technology by electrolysis method



Fig. 2 Recovery method of two Ca(OH)₂ dissolution of slag in dilute hydrochloric acid



Fig. 3 Material balance of Ca dissolution and recovery of dilute hydrochloric acid



Fig. 4 Separation techniques Ca components of the slag with sulfuric acid



Fig. 5 Material balance of slag modified with sulfuric acid

reform slag and the amount of recoverable $CaSO_4$ each per ton of slag.

4. Technology for Recovering Valuable Resources Contained in Slag Using Hydrochloric Acid

Slag that has been subjected to magnetic separation is dissolved in dilute hydrochloric acid at pH 2–3 in a tank. The reaction products are largely free CaO and complex oxides such as calcium ferrite and calcium silicate. However, only Ca is selectively dissolved in a few minutes to become CaCl₂, whereas Fe and other components of metallic oxides remain undissolved and become residues containing considerable proportions of Fe, and hence can be used as sources of iron. These residues are stripped off chlorine (Cl) by washing and used as a raw material for steelmaking.

Figure 6 shows the relationship between the concentration of hydrochloric acid and the amount of slag dissolved in hydrochloric acid and the change in solute composition. When hydrochloric acid



Fig. 6 Relationship of the main component ratio, slag dissolution and hydrochloric acid concentration

concentration is less than 1%, the amount of Ca elution is small. When it is higher than 5%, the amount of elution of Fe and Si, but not Ca, increases. It was found that when the hydrochloric acid concentration is 2%-4%, the amount of Ca elution is relatively large, while the elution of Fe and Si is restrained.

When $CaCl_2$ dissolved in hydrochloric acid is subjected to electrolysis, shown in Fig. 2, 1), Cl_2 occurs around the anode and H_2 and $Ca(OH)_2$ occur around the cathode at the same time. From the Cl_2 and H_2 generated by electrolysis, HCl can be easily produced by a chemical reaction. After dilution, HCl is reused in the slag dissolution process.

As another method of recovering $Ca(OH)_2$ without applying electrolysis to $CaCl_2$ in the hydrochloric acid solution, it is possible to precipitate $Ca(OH)_2$ through ion exchange between Ca^{2+} and Na^+ by adding NaOH solution, as shown in Fig. 2, 2). The salient characteristics of this method are as follows. First, because the pH range at which each of the hydroxides of Fe, Al, Cr, Mn, and Mg precipitates differently, it is possible to separate them more accurately and easily by gradually adding NaOH. Second, the recovery rate of $Ca(OH)_2$ is appreciably high. Third, when NaCl solution after the separation of $Ca(OH)_2$ is subjected to electrolysis to recover and reuse NaOH and Cl_2 , the electrolytic voltage is so low that the ion-exchange membrane is almost free from the formation of blisters (deposit).

Figure 7 shows the relationship between the selective dissolution of slag components and the dissolution time obtained with dilute hydrochloric acid (3.6%). Because the slag particle size was 2 mm or less, the rate of Ca dissolution after 10 minutes was $[(5.3 - 1.7)/5.3] \times 100 \approx 68\%$ and metallic components other than Ca were also dissolved, though in very small proportions.

After dissolving slag in dilute hydrochloric acid, with the maximum slag particle size of 0.125 mm, 0.250 mm, 0.500 mm, and 5.00 mm, respectively, and with the same liquid-solid ratio and reaction time, a change in the recovery rate of $Ca(OH)_2$ precipitated by NaOH addition was obtained. The result is shown in **Fig. 8**. When the maximum slag size was in the range of 0.500 to 5.00 mm, the recovery rate of Ca(OH)_2 was as low as 50%–60%. However, when the slag size was reduced to 0.250 mm and to 0.125 mm, the Ca(OH)_2 recovery rate dramatically increased to 70% and to 80%. To avoid a decline in the slag processing rate caused by refining slag particles, it is necessary to balance the cost of slag grinding with the merit of recovery of Ca(OH)_2.

Figure 9 shows the composition of the residue obtained after stirring and dissolving slag in 3.6% dilute hydrochloric acid for 10 minutes.

Figures 10 and 11 show the results of a comparison of the prop-

Dissolution trend by dilute hydrochloric acid



Fig. 7 Reaction time of slag dissolution by 3.6% hydrochloric acid



Fig. 8 Relationship between slag particle size and Ca(OH), recovery rate



Fig. 9 Slag dissolved components to dilute hydrochloric acid



Fig. 10 SEM image of Ca(OH)₂ powder, slag dissolved in hydrochloric acid

erties of Ca(OH)₂ recovered from slag and slaked lime available in the market. The SEM image reveals the presence of extremely fine, dry aggregates. Consequently, the measured particle size distribu-



Fig. 11 Particle size distribution of Ca(OH)₂ powder, slag dissolved in hydrochloric acid

tion (D50) was approximately 20 μ m. However, it is estimated that the proportion of particle sizes of 1 μ m or less was more than 50%. Compared with slaked lime or quicklime (CaO) available in the market, the particle sizes of the recovered Ca(OH)₂ are one to two factors smaller.

To compare the binder effect of raw materials for sintering, $Ca(OH)_2$ powder obtained from slag and quicklime (CaO) available in the market were mixed in such a manner that the content of Ca became the same, and the mixture was then subjected to a pelletization test using a pan-type pelletizer and drum mixer (DM). Consequently, the pan-type pelletizer provided several percent of difference in unpelletization rate and even the DM provided a little less than 1% of difference. In both the cases, the Ca(OH)₂ obtained by the immersion of slag in hydrochloric acid was slightly better in pelletizability. In the future, we plan to perform a pan test to compare their sinter productivity (expressed as a product of the sintering speed, which is associated with permeability, and the sinter yield, which is the strength index after sintering).

5. Technologies for Recycling Slag Using Sulfuric Acid

In this section, we describe the technologies for reducing slag volume and reforming slag using synthetic sulfuric acid produced by the coke plant of steelworks. In 2005–2006, our company was developing a technology for confirming the effect of a binder using $CaSO_4$ of waste gypsum board as an auxiliary sintering material on acting equipment.^{2, 3)} In the present development, using slag whose surface layer was converted into $CaSO_4$ by synthetic sulfuric acid, we studied whether it had the effect of a binder for sintering and whether it could be substituted for limestone ($CaCO_3$). The study results obtained were affirmative.⁴)

Figure 12 shows the relationship between the concentration of sulfuric acid and the composition of slag after reaction with sulfuric acid. When sulfuric acid concentration is lower than 25%, Fe elution is observed. On the other hand, when it is higher than 25%, the amount of gypsum produced decreases. Therefore, it was considered desirable that slag should be reformed using 20%–25% sulfuric acid. In addition, because aluminum sulfate was almost absent, it was found possible to remove the reformed slag of Al—an unwant-ed constituent of any raw material for steelmaking—by dissolving it in sulfuric acid. **Table 1** shows the results of a composition analysis of the slag surface layer after the slag was agitated for two hours in synthetic sulfuric acid diluted to 20%.

Figure 13 shows an SEM image of $CaSO_4$ powder of slag reformed using sulfuric acid. Figure 14 compares the particle size



Fig. 12 Relationship of the slag component and sulfuric acid concentration

Table 1 Analysis of the surface components of the sulfuric acid-modified slag

| Component | (mass%) |
|--------------------------------|---------|
| CaO | 31.7 |
| SO ₃ | 44.7 |
| Fe ₂ O ₃ | 13.0 |
| SiO ₂ | 6.11 |
| MnO | 1.17 |
| MgO | 0.913 |
| Al ₂ O ₃ | 0.565 |
| P ₂ O ₅ | 0.997 |
| | |



Fig. 13 SEM image of CaSO₄ powder sulfuric acid after modification



Fig. 14 Particle size distribution comparison of limestone and CaSO₄ of sulfuric acid after modification



Fig. 15 Comparison of SO gas concentration changes in the pot test

distribution between $CaSO_4$ of reformed slag and limestone available in the market. The particle size of $CaSO_4$ is significantly smaller than that of limestone, with a D50 of 10 μ m and a maximum size of less than 50 μ m. The reformed slag was subjected to a pelletization test using the DM. Consequently, it was determined that with a moisture content of approximately 7%, which is close to the actual operating condition, the slag reformed using sulfuric acid could safely be substituted for limestone, although there was some influence of variance in moisture content.

Following the pelletization test, a pot test was performed. Although the sintering speed based on permeability increased by approximately 10%, the sinter yield expressed by shatter index (SI) decreased by several percent. Therefore, the sinter productivity calculated as the product of sintering speed and sinter yield remained nearly the same.

In a pot test, in which sulfuric acid-reformed slag was substituted by 2% and 4%, corresponding to 20% and 40% limestone addition (about 10%), respectively, the phenomenon wherein the peak concentration of SO_x occurring in the temperature region 1050–1150°C increased 4–5 times than that with non-reformed slag was confirmed (**Fig. 15**).

In many cases, the sintering line is equipped with a desulfurizer for removing SO_x from the exhaust gas. In this case, the hourly exhaust limit for instantaneous peak must not be exceeded. Therefore, if the substitution rate of slag is approximately 0.5%, which is one digit lower than that used in the abovementioned pot test, it is considered that slag can be safely substituted, although it depends on the capacity of the sulfurizing equipment. For verification, we plan to perform a DM pelletization test and pot test.

6. Conclusion and Future Tasks

The present study is characteristic because instead of the conventional method of slag reformation using steam for hydration or carbon dioxide for carbonation, it uses waste hydrochloric acid or waste sulfuric acid with dissolved Fe that occurs in large volumes within steelworks (in a downstream process) or coke-derived synthetic sulfuric acid that has increased in volume with the increase in the sulfur content of coking coal in recent years.

The abovementioned acids are inexpensive and may require some treatment. Even so, the treatment equipment required is relatively simple because heat is not required. Moreover, the developed technologies are applicable not only to slag but also to dust, fly ash, waste refractories, etc., containing Ca and Fe to recover their useful components. 1) Technologies for recovering useful components of slag using hydrochloric acid

We developed the world's first integrated technology wherein Ca in slag is selectively dissolved in waste dilute hydrochloric acid to obtain CaCl₂, which, after filtration of the residue, is directly subjected to electrolysis to recover Ca(OH)₂ and Cl₂; Cl₂ is then used in the production of hydrochloric acid. At the same time, we successfully developed a new technology wherein the Ca-dissolved hydrochloric acid solution after filtration of the residue is subjected to pH adjustment using NaOH to allow recovering of Fe, Al, Mn, Mg, etc. (other than Ca), which are precipitated in the form of hydroxides at pH < 10.5, and for recovering high-purity, fine-grain Ca(OH)₂ at pH > 10.5.

2) Technology for recycling slag using sulfuric acid

In addition, we developed a technology for converting the surface layer of slag into gypsum $(CaSO_4)$ using waste sulfuric acid or surplus sulfuric acid from a coke plant for using the reformed slag as a binder for pelletizing raw materials for blast furnace or as a source of Ca. Because slag components other than Ca can be dissolved in sulfuric acid, technology for recovering Fe, P, and other useful elements from the abovementioned sulfuric acid solution has also been developed.

In the technologies for recycling slag using acids, the problems that remain to be solved are as follows.

- 1) For waste hydrochloric acid from the pickling and other such processes, the following are required.
- Efficient method of grinding slag to increase the amount of Ca dissolution
- Technology for transporting and cutting ground slag
- Efficient dehydration technology to allow multiple stages of filtration
- Technology for efficient washing/removal of Na and Cl
- Technology for efficient drying/grinding of slag
- 2) For waste sulfuric acid or coke-derived synthetic sulfuric acid, the following are required.
- Securing a stable supply of surplus sulfuric acid because at present sulfuric acid cannot be recycled
- Method of treating sulfuric acid solution after removing Fe and PO_4^{3-}
- Determining the amount of SO_x generated in the process of sintering blast furnace raw materials
- Conducting a comparative study of the cost of recovery of SO_x, the cost of chemicals for neutralizing sulfuric acid, and the effect of Ca substitution for blast furnace raw material.

In the future, we intend to solve the abovementioned problems, start up a pilot plant for the study of scale-up of these technologies, and complete the evaluation of investment vs. effect by the year 2016 so as to establish, by around 2019, a technology for treating at least thousands of tons of slag per year at multiple steelworks of our company, if possible. This will not be attainable by the Advanced Technology Research Laboratories alone. Therefore, close cooperation is indispensable with the Head Office/Process Engineering Div./ Water Treatment Engineering Dept., the Civil Engineering & Architectural Research Div./Slag Engineering Dept., the Slag Depts. of Steelworks, Nippon Steel & Sumikin Engineering Co., Ltd./Technology Development Research Lab. I/Steelmaking Plant Div., etc.

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