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Recycling of some steel industrial solid wastes for high-value material applications

Cui PENG, Xin ZHI, Minyuan GU, Ruifei HE, Zhancheng GUO

Key Lab. of Ecological & Recycling Metallurgy, University of Science & Technology Beijing (USTB), China

zcguo@metall.ustb.edu.cn

Abstract

The successful valorisation of the waste generated in the steel industry requires innovative technologies, which may bring both economic and environmental advantages. This paper conceptually introduces three process methods for making high-value materials from steel industrial solid wastes, i.e. the white carbon black production from the dust generated in the ferrosilicon production plant, the recovery of potassium chloride from sintering dust of ironmaking works, and the sound-absorbing material preparation from iron-making slag.

Introduction

Steel production is associated with a significant accumulation of wastes, such as slag, sludge and dust. Some of these can be economically recycled: *e.g.* ironmaking slag as cement raw material. Others cannot yet be recycled due to technical and economic reasons, which need innovative technologies in order to reduce the environmental impact. However, the present, existing technologies to recycle metallurgical wastes are only applicable for low value utilisation, which hinders its wide application. In this paper, three processing methods to reutilise metallurgical wastes are proposed to prepare different high value materials according to the distinct chemical and physical properties of the wastes.

White carbon black preparation from the dust of ferrosilicon plant

The “heavy pollution industries”, such as ferroalloy, CaC_2 and PVC plants are generally located in the area close to the coal mine. In a ferrosilicon plant, silica fume is generated at about 100~200 kg per tonne of Fe-Si alloy.The size of this silica fume is below 10 µm while the wt% of SiO_2 exceeds 80%. Little of silica fume can be used, due to its complex constituents. On the other hand, for PVC production a large amount of waste water containing 20~30% NaOH is generated from chlorine gas production works. On the other hand, a large amount of flue gas with a high content

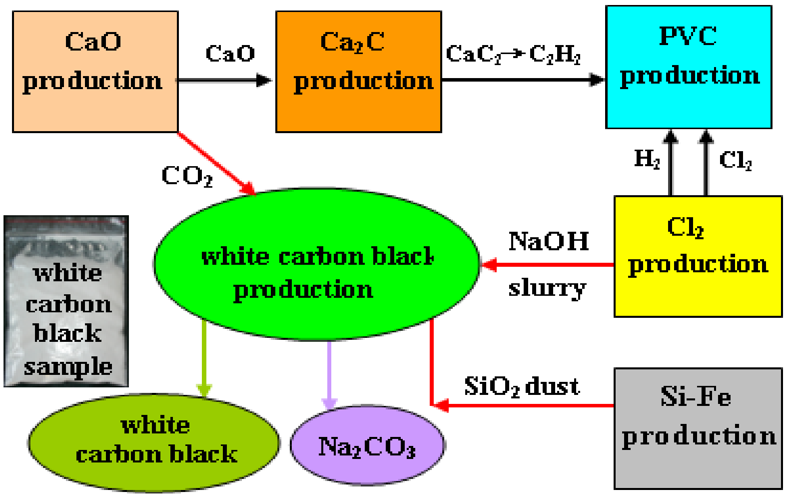


Figure 1 The conceptual design of an interlinkage technology for ferroalloy, calcium carbide and PVC production in environmental-friendly way

of CO_2 is generated in lime production works. To improve the environmental situation of these heavy pollution plants and to economically recycle their wastes, a novel recyling process has been proposed (Figure 1), which produces white carbon black and Na_2CO_3. The pilot experiments shows that the quality of the white carbon black produced through the present proposed method is better than that by the traditional precipitation method using sodium silicate with sulfuric acid, and is comparable with that by the CVD method using silicon chloride.

The principle is that NaOH containing waste water (generated in Cl_2 production) reacts with silica fume (generated in the ferrosilicon production) forming Na_2SiO_3 solution at low temperature due to the high activity of silica fume:[1]

$$2NaOH+SiO_2 \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

Subsequently, the filtered Na_2SiO_3 solution reacts with CO_2 (generated in lime production), forming micro-nano SiO_2 crystals (white carbon black) and Na_2CO_3 solution, as expressed by reactions (2) and (3). The white carbon black product is a high value chemical product, which is commonly used in the rubber industry, while Na_2CO_3 is also a valuable chemical product. [2]

$$Na_2SiO_3+CO_2+H_2O \rightarrow Na_2CO_3+H_2SiO_3\downarrow \quad (2)$$
$$H_2SiO_3 \rightarrow SiO_2.nH_2O\downarrow \quad (3)$$

Figure 2 schematically shows the process of white carbon black production by silica fume, generated in the ferrosilocon plant, with NaOH offal liquid from the chloralkali

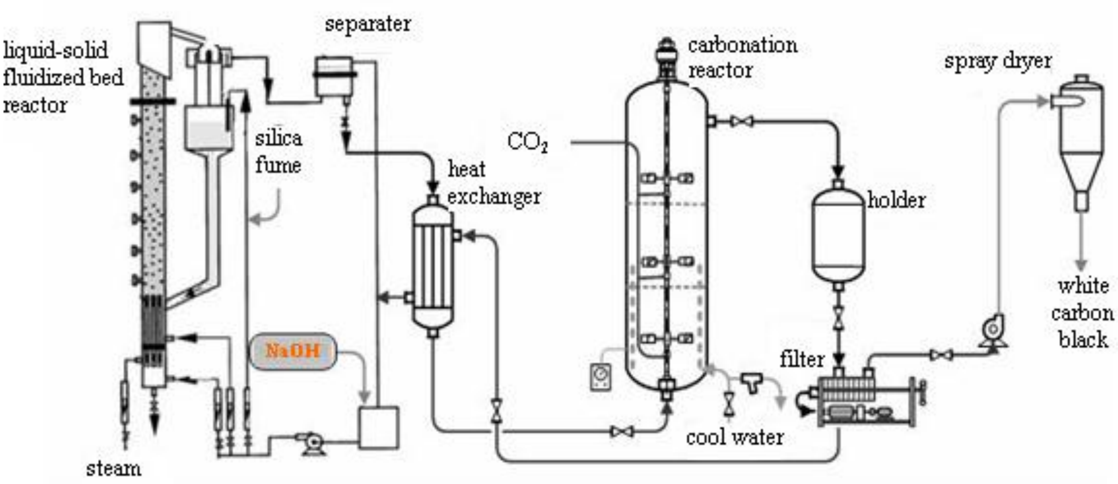


Figure 2: Schematic diagram of white carbon black production by silica fume from the ferrosilicon production plant with NaOH offal liquid from the chloralkali production plant and CO_2 flue gas from the lime production plant

plant and CO_2 flue gas from the lime production plant. The temperature for the silica fume dissolution reaction (by NaOH) to form sodium silicate is controlled at about 150^{o}C. The temperature of the carbonation reaction is controlled at approximately 80^{o}C to obtain the appropriate specific BET surface area and DBP sorption rate of the white carbon black product for its usage in the rubber industry. The effect of the carbonation reaction temperature on BET specific surface area and DBP sorption rate of the white carbon black product is shown in Figure 3.[3]

In 2010, a pilot plant producing 1500 tonnes/year of white carbon black product was constructed, demonstrating that the above proposed process was applicable. The industrial production plant with a 10000 tonnes/year capacity is constructed in the Erdos Metallurgy Group of China.

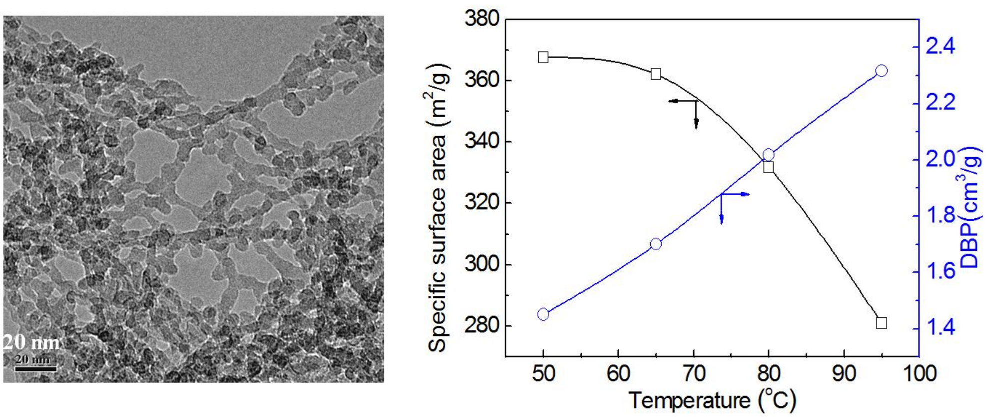


Figure 3: Structure of the white carbon black and effect of the carbonation reaction temperature on the BET surface area and DBP sorption rate of the product (conditions: 33% CO_2, 40 g/L Na_2SiO_3)

Recovery of potassium chloride from sintering fume of ironmaking works

The sintering fume collected by the electrostatic precipitator (SEP) in an iron ore sintering plant in the steel industry contains more than 30% potassium chloride,[4] which cannot be recycled within the steel plant due to its high content of potassium chloride. Approximately 3~4 kg of this dust is generated per tonne of pig iron production.

In addition, the total amount of the flue dust accounts for 8-12% of the steel output.[5] Most of these dusts not only contain high Fe and C contents, but also contain Zn, Pb, K and Na to some extent. Returning these dusts directly to the sinter plant for recovering Fe and C is not a sound option, as Zn, Pb, K and Na would be concentrated. Eventually this would jeopardise the normal blast furnace operational practice. In recent years, RHF (rotary hearth furnace) is used as an effective method for treating metallurgical dust, which contains an attractive amount of Fe and C. This RHF method does not only reduce iron oxides into metal Fe with C as reduction agent,[5] but also removes Zn, Pb, K and Na from the dust. In the RHF process, there is also fume released, called the second fume, which adds up to a level of approximately 100 kg per tonne of treated dust. This second fume typically contains approximately 40% of ZnO + PbO and 20% of KCl.[6]

Metallurgical fumes containing K are considered as a valuable resource in China due to the extreme scarcity of potassium, which is required for potassium fertiliser production. Figure 4 schematically illustrates the process for the removal of Zn, Pb, K,

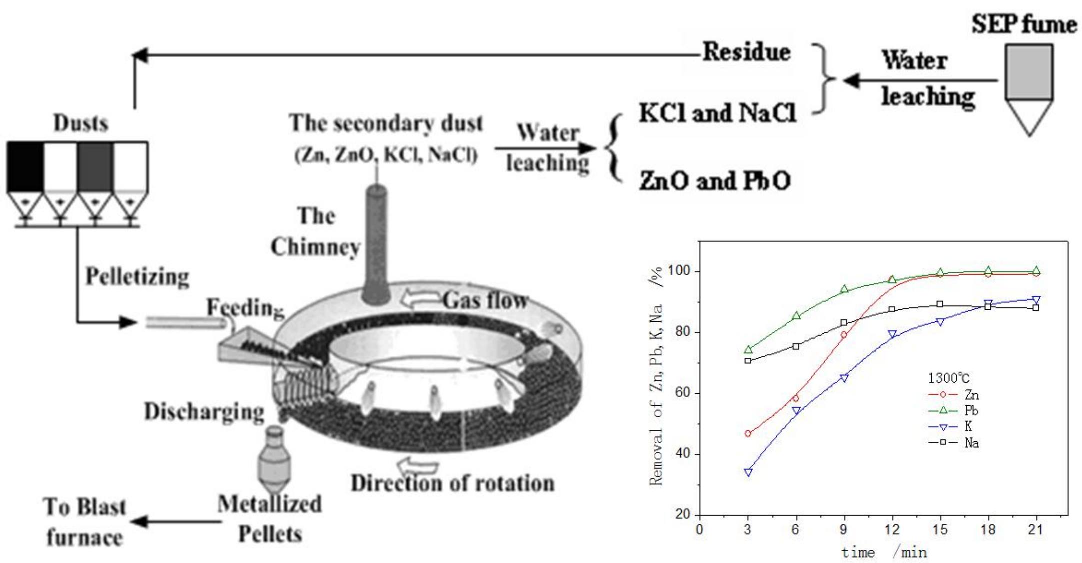


Figure 4: Schematic diagram of recovering potassium chloride from metallurgical dust.

and Na from metallurgical dust by the RHF. Using lab-scale RHF experiments, the effect of temperature on their removal rate was investigated. The results show that the removal rate of Zn, Pb, K, Na are faster when the temperature is higher, and the removal percentages (of all elements) reached maximum value within 30 min in the temperature range of 1200 to 1330°C. Removal percentages of the elements Zn, Pb, K and Na exceed 90%.

The process of recovering KCl from the SEP and RHF fumes is schematically shown in Figure 5.[7,8] This process can be divided into three stages, being extracting, evaporating and crystallisation. For the first stage, the SEP fume was fed to the extracting tank followed by adding a proper amount of tap water, and stirring at about 90°C. Afterwards, the leaching liquor was separated from the residual with a filter. The leaching process is to be accomplished by countercurrent leaching using multi-steps. After the liquid/solid separation, the leaching residual with enriched Fe and C is released from the bottom of the tank and returned to the sinter plant for reuse. The leachate obtained through the four-stage countercurrent leaching is prepared for heavy metals removal, which is also processed in the leaching tank. The liquid/solid separation in this step is completed in the same way as in the leaching

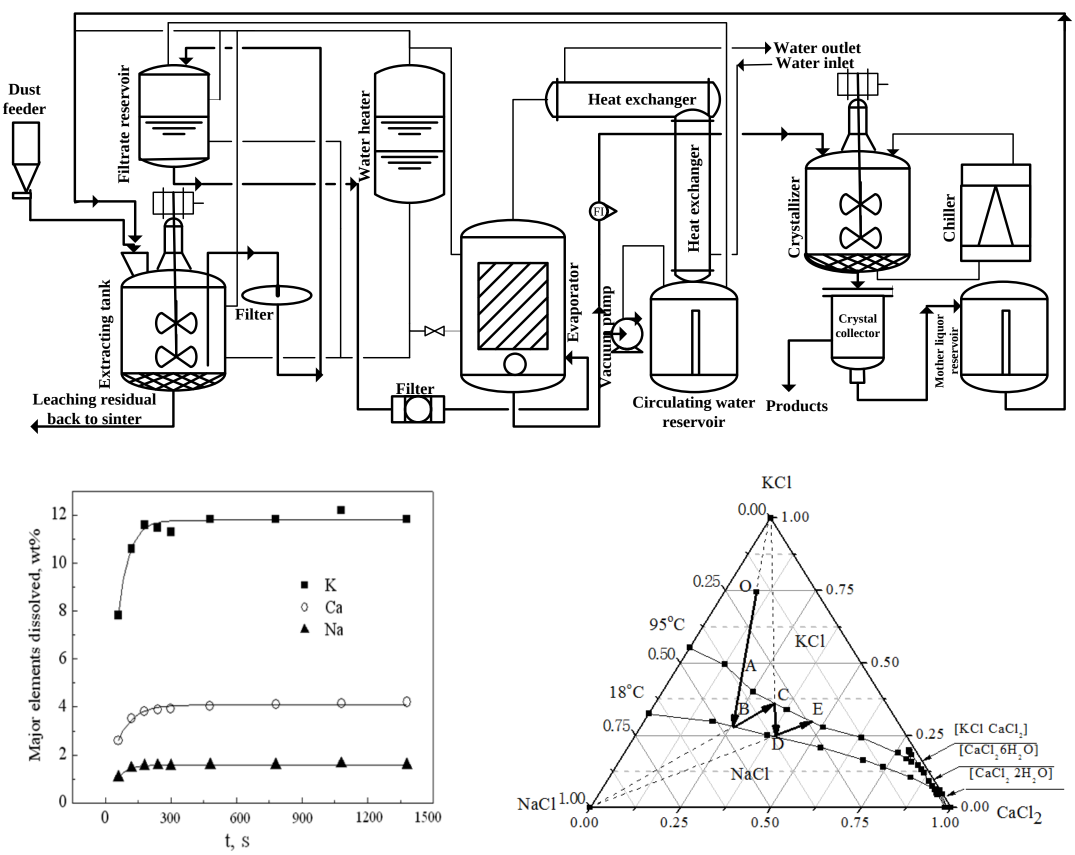


Figure 5 Schematic diagram of the extraction process of KCl from metallurgical fume.

step. The separated liquor is directly transported into the evaporating tank with the help of a vacuum air pump. In the evaporating process, the extracted and purified leaching solution containing a small amount of impurities is further concentrated under a certain vacuum condition. Subsequently, the concentrated solution is transported to the crystalliser. The coolant for the crystalliser is provided by a chiller. Finally, the crystalline product is collected in a small tank with a filter, and the mother liquor is transported to a special reservoir before returning it to the extracting tank.

Pilot tests showed that more than 90% of potassium chloride can be recovered and the purity of the recovered potassium chloride can reach over 95%. This method is expected to provide about 20% of the potassium chloride demand in China.

Sound-absorbing material preparation from iron-making slag

Water-granulated slag is a by-product of ironmaking works. Its amount is about 300 kg per tonne of pig iron. Currently, it is usually employed as a raw material for the cement industry. The slag with rich pores and good sintering properties is easy to form blocks with high stress. It is well known that a sound-absorbing panel is a material with a porous structure. Therefore, it is possible to produce sound-absorbing material by using the water-granulated ironmaking slag.

The currently available sound-absorbing porous materials have different drawbacks, *e.g.* weak fireproofing property for organic fiber, and environmentally-unfriendly.

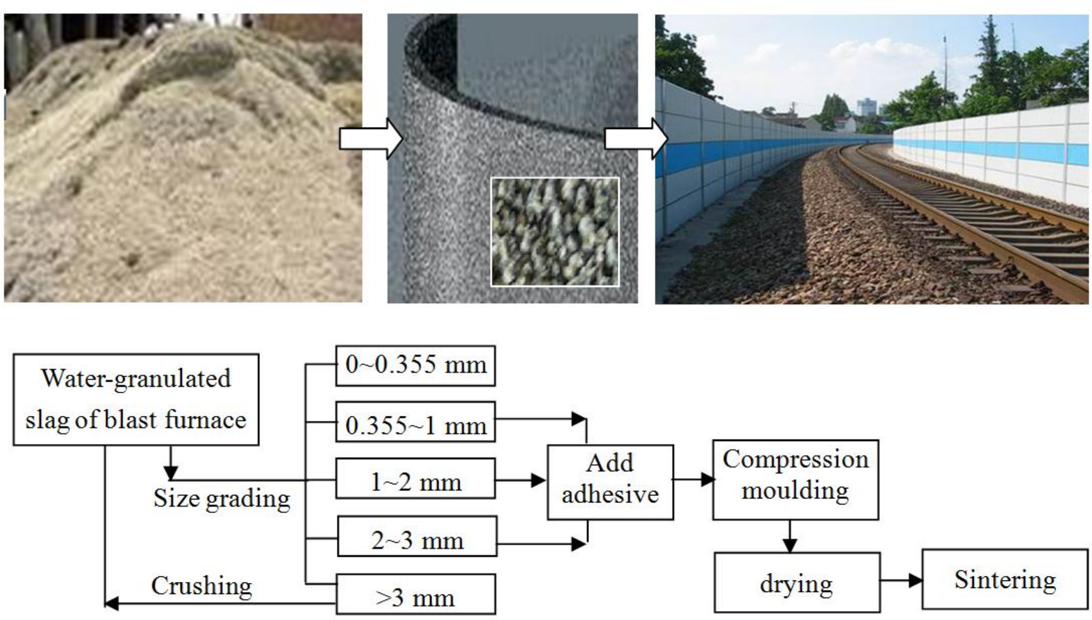
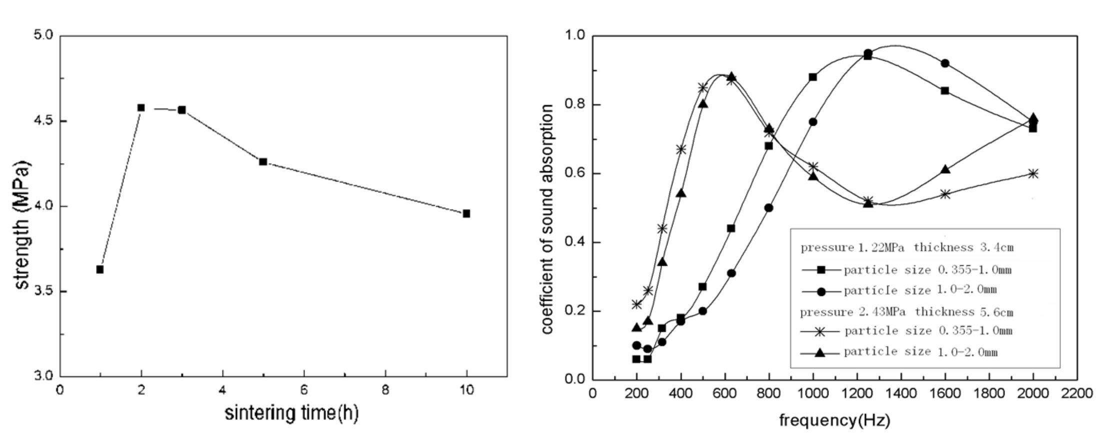


Figure 6: Schematic diagram of sound-absorbing material made from ironmaking slag

Although the metal sound-absorbing material possesses excellent sound-absorbing properties, its application is restricted due to its high production costs. If the water-granulated ironmaking slag can be used as the raw material of sound-absorbing porous material, it will be an excellent substitute with good application prospects because of the strong competitive price of the water-granulated ironmaking slag.

Sound-absorbing panels were prepared by using a high-temperature sintering process. A standard sample (cylinder with diameter of 10 cm) was prepared by compressive forming and sintering at the temperature of 1100°C.[9] Subsequently, the sound absorption coefficient of the sample was measured by the standing wave tube method.

The relationship between sintering time and compression strength of the samples (thickness 3.4 cm, slag size 1~2 mm) is shown in Figure 7(a). It can be seen that when the sintering time was 2~3 h, the sample has the highest compression strength, with the average strength reaching more than 4.5 MPa. The average strength could be about 5.0 MPa if the slag size is 0.355~1 mm and sintering time is 2~3 h. Figure 7(b) shows the sound absorption coefficient of the samples sintered for 2 h. The samples (thickness 3.4 cm) made of smaller slag particle size possess better sound absorption properties. This suggests that they have a larger average sound absorption coefficient and also larger sound absorption coefficient in the low frequency spectrum, with respect to samples made of a bigger slag particle size, when the sample preparation pressure was 1.22 MPa. This is because samples made of smaller particle size have a bigger flow resistance due to more pores and a smaller pore diameter. When the sample preparation pressure was raised to 2.43 MPa, samples (thickness 5.6 cm) made of water-granulated ironmaking slag in the two particle size ranges (“the two particle size ranges” for short below) have a similar average sound



a) b)

Figure 7: Effect of sintering time on strength (a) and effect of slag particle size on sound absorption properties (b)

absorption coefficient of around 0.5800. This is because samples made of the smaller particle size range are more likely to form closed pores, which exert negative effects on the sound absorption properties. The sound-absorbing porous materials made of the two particle size ranges both have good sound absorption properties, suggesting it is feasible to use the water-granulated ironmaking slag as raw material for sound-absorbing porous material.

Conclusions

This paper introduced three examples of industrial symbiosis. Firstly, taking advantage of the high activity of silica fume generated in the ferrosilicon plant, white carbon black can be produced by using the silica fume with NaOH offal liquid from a chloralkali plant and CO_2 flue gas from a lime production plant. This innovative technology enables not only a significant improvement of the environmental situation for ferrosilicon, chlorine gas and calcium carbide production, but also generates a successful reutilisation of the wastes produced from these industries. Secondly, the sintering fume arrested by the electrostatic precipitator in the iron ore sintering plant and the secondary fume from RHF for treatment of metallurgical dust in steel industry contains a high content of potassium chloride up to about 20%, which can be used to produce potassium chloride by a hydrometallurgical process. Thirdly, water-granulated ironmaking slag with rich pores, sintered at 1100^{o}C, has good sintering properties and can be used to make sound-absorbing porous material. The material has good sound-absorption properties with average sound absorption coefficient over 0.70 and compressive strength up to 5.0 MPa.

Acknowledgments

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