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Recycling of Fly Ash and Industrial Waste as Sinter ore During Metallurgy Process

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Fly ash is classified as a hazardous waste. So it should be specially treated. Industrial waste from Iron and Steel Co. containing blast furnace dust, converter dust, pyrite cinder and mill scale *etc*., should also be treated before disposal. However, specific research on both fly ash and industrial waste in a work was rarely reported. In this paper, sinter ore was made from fly ash with the addition of industrial waste by metallurgy process. The results showed the produced sinter ore met strength and metallurgical properties standard. And the leaching concentration of sinter ore was lower than the Chinese regulatory thresholds.

Key Words: Fly ash, Industrial waste, Metallurgy process, Leaching toxicity.

INTRODUCTION

Fly ash is a challenge not only because it has few uses and contains a considerable amount of water-soluble material, but more importantly because it contains a number of environmentally hazardous species[1-3]. These include the heavy metals and the chlorinated organic. The main difficulty with fly ash is that most of the lead and most of the chromium as well as a large amount of zinc are in an easily leachable form. Therefore, these metals must either be removed or immobilized if fly ash is to be made environmentally safe.

In China, cement solidification is usually applied to the fly ash treatment. However, this technique is limited due to the high concentration of chlorine compounds present in the forms of dioxins and alkali chlorides. By cementation or chemical treatment, it is difficult to destroy or immobilize dioxins[4] and alkali chlorides hinder hydration of cement. Although, landfill is known to be the most convenient and inexpensive method of the solid waste disposal, the best method for fly ash treatment is recycling and reuse from the view point of long-term sustainability.

On the other hand, steel industry generates a lot of waste materials such as iron ore fines, mill scale, flue dust, stock house dust and lime dust *etc*. The industrial waste is generally disposed at prescribed areas by public institutions[5-9]. The recovery of these by-products becomes more and more important as legal requirements demand for a through utilization, existing landfill capacities as well as primary resources become scarce and rising prices for metals make such an utilization economically attractive.

In the literature, more attention has been to fly ash and industry residues. However, specific research on both fly ash and industry residues in a work was rarely reported[10-13]. The aim of contribution is to produce available resource using fly ash and industry waste which are solid waste. The process comes from and Steel Co.-pellet process and sintering process and the energy using treating fly ash produced by the steel production process. So it was not only saving energy but saving natural resources and preventing waste through this sustainable approach. This paper concerns physical properties, metallurgy properties and leaching toxicity of produced sinter. The results showed higher strength and better metallurgical properties and the leaching toxicity of produced sinter met the regulation.

EXPERIMENTAL

Fly ash used in this study was from Chongqing Tongxin MSW Incineration Plant (Chongqing, China). The major chemical composition of the fly ash was given in Table-1. On the left, the major elements expressed were oxides. Their abundances were very common. In contrast, the species on the right hand side were very unusual and were the environmentally important species.

Rest materials: Blast furnace dust, converter dust, pyrite cinder, iron ore, limestone, quick lime, coke breeze, returns and mill scale, were very common and supplied by Chongqing Iron & Steel Co. (Chongqing, China) and the major chemical compositions of these materials were given in Table-2.

Sintering tests: The flowchart for sintering tests was shown in Fig. 1. First, granulation was conducted by granulator

TABLE-1
CHEMICAL COMPOSITION OF THE FLY ASH (%)

Major elements as oxides	wt. %	Other elements	wt. %
SiO_2	15.24	Cl^-	8.37
Al_2O_3	5.7	Zn	0.4653
Fe_2O_3	4.83	Pb	0.1481
CaO	23.79	Cr	0.1356
MgO	4.17	Cu	0.0623
K_2O	3.86	Mn	0.0915
Na_2O	7.29	SO_3	8.16
TiO_2	1.02	–	–
Other	17	–	–

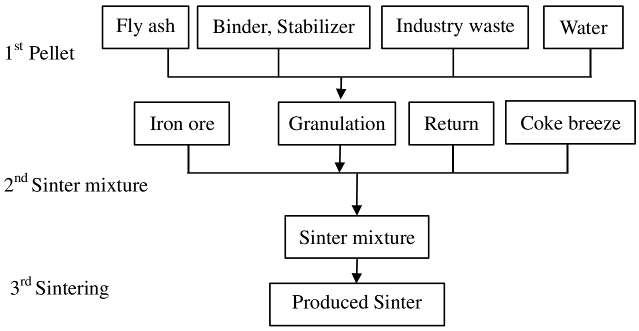

Fig. 1. Flowchart for sintering tests

and then sinter mixture was also need to prepare. Finally, the granulation of sinter mixture was loaded into sinter pot with the thickness of 600-700 mm. after ignition at 1050 ± 50 ºC for 2 min, sintering proceeds until the end point of sintering when the temperature of flue gas reaches the peak value, then cooling was followed.

Methods of analysis: Tumble index and abrasion index of sinter were measured according to GB 8209-87. Reducibility and reduction degradation index of sinter were measured according to GB/T 13242-91[14].

Toxicity characteristic leaching procedure: Leaching toxicity of heavy metals was determined, according to the Chinese Standard Method, for leaching toxicity of solid wastes rollover leaching procedure (GB50086.1-1997). Firstly 40.0 g dried sample (< 5 mm particle size) was mixed with 400 mL deionized water in a 1000 mL polyethylene bottle, at a solid to liquid ratio of 1:10; secondly, the bottle containing the mixture was fixed in a rolling agitator and rolled at a speed of 30 rpm for 18 h continuously, then it was left for settle down for 0.5 h; thirdly, the soluble component was separated by vacuum filtration, using a filtrate membrane with 0.45 µm micropores. Finally, the filtrate was adjusted to a given volume and then the concentrations of heavy metals in it were determined by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Influence on strength: The test of sintered ore strength describes a method for evaluating the tumble strength of the iron ores by determining the tumble index and abrasion index. The tumble index, which presents the room temperature strength of the sinter and gives an indication of its disintegration behaviour during handling, is computed as the percentage + 6.3 mm. The abrasion index is computed as the percentage - 0.5 mm.

According to the regulation, all the examined sinters must conform to the requirements of tumble index (% + 6.3 mm) > 60 % and abrasion index (% - 0.5 mm) = 5 %/min. As shown in Table-3, the sinter tumble index and abrasion index improved when adding fly ash. The better strength of sinter was beneficial to decrease weight loss in transit, which led to better permeability and better stability of blast furnace material column.

Influence on reduction degradation index (RDI): The reduction degradation index (RDI) is used as one of the most important indices to represent the behaviour of sinter in the furnace during the iron making process. Improving RDI of sinter decreases the fines and dust generation during their reduction, so improving the bed permeability. Improved permeability increases the productivity of the iron making unit. As shown in Table-3, produced sample RDI + 3.15 is lower than RDI + 3.15 of base case (reference material from Chongqing Iron & Steel Co.). This is a result of the sinter structure at higher basicity, which is distinguished by a continuous ferrite frame capable of arresting the propagation of cracks initiated at the hematite crystal. The addition of fly ash also results in a higher sinter FeO, thus having an effect equivalent to that of the coke addition. Although adding fly ash decreased RDI + 3.15 of produced sinter, it still met the limitation.

Influence on reducibility (RI): The reduction degree is an important factor affecting sinter quality. Unfavourable reducibility (RI) decreases blast furnace efficiency. Reducibility (RI) depends on physical and chemical characteristics of the sinter. The influence of fly ash on reducibility characteristics is shown in Table-3, Comparing with reducibility (RI) of base case, it can be seen that the reducibility (RI) of sinters was improved. The positive influence of fly ash addition on

TABLE-2
CHEMICAL COMPOSITION OF INDUSTRIAL WASTE (%)

	TFe	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	S
Returns	53.30	6.33	2.16	8.20		11.08	0.08
Mill scale	13.10	16.67	6.95	5.10	11.83	32.60	0.25
Blast furnace dust	52.13	9.58	2.70	–	33.53	5.44	–
Converter dust	51.46	2.24	0.45	47.79	–	12.39	0.12
Pyrite cinder	63.05	6.59	–	0.38	–	1.12	0.23
Iron ore	65.87	3.56	0.93	44.91	43.00	3.20	0.06
Limestone	0.90	2.56	0.88	–	–	52.28	0.08
Quick lime	0.50	4.54	0.94	–	–	83.23	0.14
Coke breeze	10.80	49.40	27.00	–	–	3.45	0.79

TABLE-3
INFLUENCE ON SINTER PROPERTY (%)

	FeO	TI	AI	RI	$RDI_{+3.15}$
Base case	7.72	73.40	3.88	89.28	73.89
1#	7.07	76.86	4.07	93.06	59.36
2#	7.07	80.31	3.97	92.84	58.34
3#	7.39	81.86	4.32	91.52	59.62
4#	7.14	83.58	4.65	89.85	57.96
5#	7.65	79.31	4.28	93.83	60.06

Base case: Using the sample as reference material from Chongqing Iron & Steel Co. (Chongqing, China), its propriety was considered the standard. 1#, 2#, 3#, 4#, and 5#: the five samples was added fly ash.

the reducibility (RI) of sinter is believed to be a result of the increase in hematite and calcium ferrite phases and decrease in magnetite phases having higher reducibility.

Toxicity characteristics leaching procedure (TCLP) tests of sinter ore: Metallurgy process was found to decrease the leaching concentrations of the samples, as shown in Table-4. The leaching concentrations of heavy metals were lower than Chinese regulatory thresholds. According to the research by Pan *et al.*[15], heavy metals should be embedded in the unsaturated polyester glass, usually, most of the heavy metals could be fixed in this net-like structure, thus were not easy extracted. Based on these results, the leaching concentration for the target metals could meet the Chinese regulatory thresholds well.

TABLE-4
LEACHABLE TOXICITY OF SLAG (mg L^{-1})

	Cr	Cd	Cu	Zn	Pb
1#	0.150	0.086	0.089	0.030	0.184
2#	0.155	0.092	0.118	0.024	0.160
3#	0.141	0.081	0.103	0.030	0.191
4#	0.156	0.084	0.100	0.025	0.148
5#	0.141	0.083	0.108	0.029	0.195
Regulation standards	10	0.3	50	50	3

Conclusion

Sinter ore was made form metallurgical materials and fly ash and then physical properties, metallurgical properties and leaching toxicity of sinter were investigated and analyzed. Tumble strength and reducibility improved obviously. As for reduction degradation index, the value was lower than reduction degradation index of base case. In addition, the leaching data of heavy metals from leach tests met the regulatory thresholds. Fortunately, the result showed this method not only disposed fly ash safely but also had no negative effect on metallurgy process, which provide a new way for fly ash and industrial waste.

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