4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

THE RECOVERY OF ZINC FROM STEEL DUST BY USING SUBMERGED INJECTION SMELTING PROCESS

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Synopsis : In the present study, the method of submerged injection smelting process was done to eliminate Zn and Pb from Steel-Dust with vaporization. To investigate the effect of temperature on the Zn vaporization rate three temperatures of 1473K, 1523K, and 1573K were chosen. As the temperature increased the Zn vaporization rate increased. The Zn contents of silicate slag and calcium-silicate slag decreased rapidly for 30 minutes after gas injection and decreased slowly after 30 minutes, respectively. The Pb contents in the slags also decreased rapidly for 30 minutes and decreased slowly after 30 minutes, respectively. This is the reason why the amounts of ferric and ferrous vary in the slags.

Key words : steel dust, submerged injection smelting process, calcium-silicate, slag, nitrogen, reductant, flux.

1. INTRODUCTION

The steel dust produced from electric arc furnace steelmaking plants includes 15-25%Zn, 3-4%Pb, 4-6%Cl, and etc. Although the steel dust treating methods were not fully understood , several methods were proposed so far. Those are the Waelz process (1), plasma reduction smelting process, iron reduction distillation process (2) and etc.

The Waelz process has many difficulties in Zn and Pb recovery and also has some special environmental problems. The plasma smelting reduction process using extremely high temperature has not been industrialized due to the difficulties in treating large amount of steel dust. In the iron reduction distillation process, hematite is reduced into iron by the injection of CO gas, and Zn is recovered by the reaction of the reduced iron and ZnO. However, this process also is not used in practical plants.

Considering all these problems, the present study is done to recover Zn and Pb from steel dust using submerged injection smelting process (3),(6) and to make the residue into the slag suitable for the raw material of cement.

2. EXPERIMENTAL

The chemical compositions of steel dust used in this study are listed in Table 1. Table 1.

(1) is the composition of the original steel dust and Table 1.(2) is that of the steel dust after dechlorining up to 91%. Dechlorination was done by agitating the solution of 200g of steel dust per liter of distilled water. Fig.1 represents the schematic diagram of the apparatus used in this experiment. The charged steel dust was melted with the reductant and the flux(SiO_2, CaO) in a magnesia crucible at 1523K, and nitrogen gas was injected into the liquid using a stainless lance. So Zn, Pb, Cl, and etc. were vaporized and collected in the dust collector. With the preliminary experiments, the suitable slag composition was selected considering the fluidity of slag and the condition of gas injection for each experimental temperature. In order to determine the optimum vaporization condition of Zn and Pb from the silicate slag and calcium-silicate slag, the vaporization rate of Zn and Pb was investigated with the amount of gas, the amount of coke, and the gas injection time. Samples were analyzed by A.A. and titration method.

Table 1. Compositions of steel dust (Wt%).

	Zn	Pb	T.Fe	Cu	Cd	S	F	SiO_2	Cl	CaO	C	Ag ppm
(1)	22.62	4.18	31.75	0.24	0.04	0.57	0.31	3.14	3.43	1.74	4.96	102
(2)	20.41	3.90	33.21	0.27	0.03	0.41	0.32	3.78	0.31	1.78	0.40	105

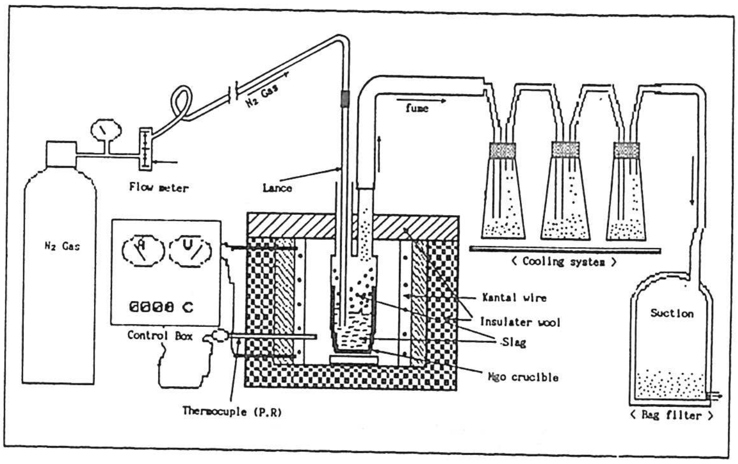

Fig.1. Schematic diagram of experimental apparatus.

3. RESULTS AND DISCUSSION

1. The reaction of smelting reduction

The fundamental reactions of smelting reduction of steel dust are summarized in Table 2 with the standard free energy. Figs.2 and 3 represent the change of Zn and Pb content in the 70%FeO-30%SiO_2 slag and 65%FeO-25%SiO_2-10%CaO slag with 2%carbon under gas injection rate of 5 l/min. for 90minutes. The Zn contents of silicate slag and calcium-silicate slag decreased rapidly up to 1.0% for first 30 minutes after gas injection, and those were 0.02% and 0.03% after 90 minutes, respectively. The Pb contents in the slags also decreased rapidly up to 0.1% for

Table 2. Standard free energy of reaction at 1523 K.

Reaction	ΔG° (J) $^{9.10.11.12.13.16)}$	
$C_{(s)} + 1/2\ O_{2(g)} = CO_{(g)}$	-111960 - 87.78 T	(1)
$2CO_{(g)} + O_{2(g)} = 2\ CO_{2(g)}$	- 564840 + 173.3 T	(2)
$C_{(s)} + CO_{2(g)} = 2CO_{(g)}$	170460 - 174.43 T	(3)
$Fe_2O_{3(s)} + CO_{(g)} = 2FeO_{(s)} + CO_{2(g)}$	2515 - 34.93 T	(4)
$ZnO_{(s)} + C_{(s)} = Zn_{(g)} + CO_{(g)}$	348480 - 286.10 T	(5)
$ZnO_{(s)} + CO_{(g)} = Zn_{(g)} + CO_{2(g)}$	178020 - 111.67 T	(6)
$PbO_{(l)} + C_{(s)} = Pb_{(m)} + CO_{(g)}$	83140 - 165.48 T	(7)
$PbO_{(l)} + CO_{(g)} = Pb_{(m)} + CO_{2(g)}$	- 87320 + 8.95 T	(8)
$ZnO_{(s)} + 2FeO_{(s)} = Zn_{(g)} + Fe_2O_{3(s)}$	175505 - 76.74 T	(9)
$PbO_{(l)} + 2FeO_{(s)} = Pb_{(m)} + Fe_2O_{3(s)}$	- 89835 + 43.88 T	(10)
$ZnO_{(s)} + 3FeO_{(s)} = Zn_{(g)} + Fe_3O_{4(s)}$	162854 - 92.48 T	(11)
$PbO_{(l)} + 3FeO_{(s)} = Pb_{(g)} + Fe_3O_{4(s)}$	62790 - 50.65 T	(12)

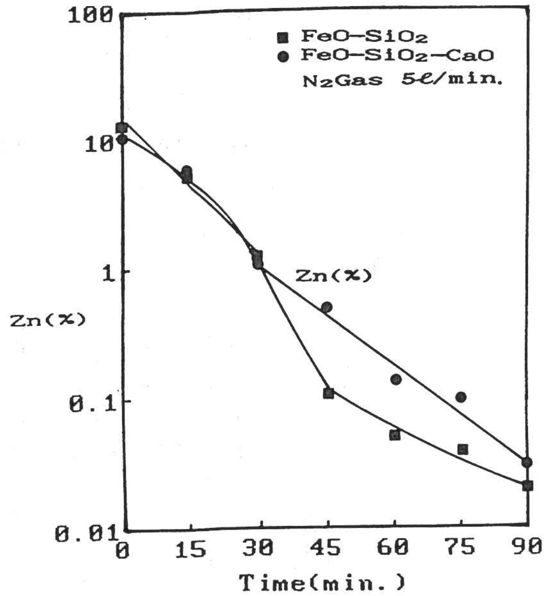

Fig.2. Change of zinc in slags with gas injection time at 1523 K.

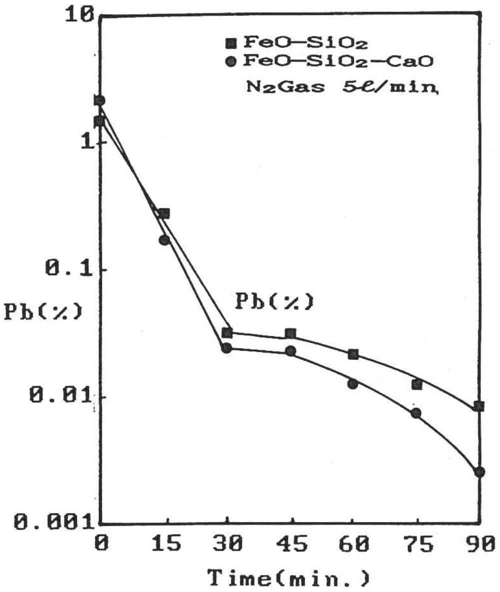

Fig.3. Change of lead in slags with gas injection time at 1523 K.

30 minutes, and those were 0.01% and 0.05% after 90 minutes, respectively. Fig.4 shows the amount of Fe^{3+} in the slags rapidly increased with the gas injection time up to 30 minutes. Thus, the decrease of Zn and Pb in the slags can be explained with the equations (9),(10), (11), and (12) in Table 2. After 30 minutes, the vaporization rate of Zn, Pb, and Fe^{3+} decreased probably due to the reduction by carbon. The vaporization rate of Zn was larger in the silicate slags than in the calcium-silicate slag as reported by Banya et al. (4). According to Yazawa et al. (5), as the ferric-ferrous ratio increased, the vaporization rate of Pb decreased. Figs. 5and 6 represent the change of Zn content with nitrogen gas flow rate for silicate slag and calcium-silicate slag, respectively. The vaporization rate of Zn increased with nitrogen gas. However, the final Zn content in the slags is not changed regardless of the gas flow rate. To investigate the effect of temperature on the Zn vaporization rate, three temperatures of 1473K, 1523K, and 1573K were chosen. The changes of Zn content with temperature for each slag are shown in Figs.7 and 8, respectively. As the temperature increased the vapor pressure of Zn(P_{Zn})

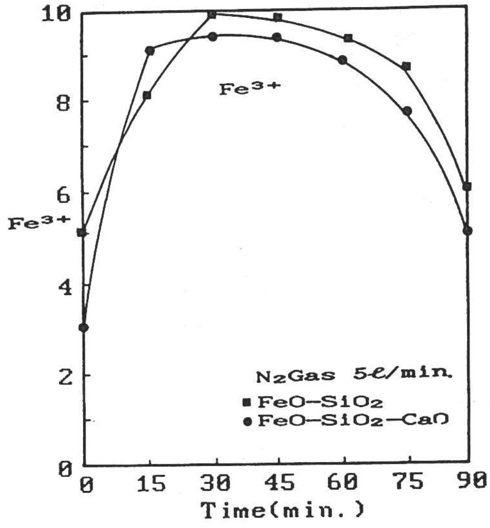

Fig.4. Change of Fe^{3+} in silicate slag with gas injection time at 1523 K.

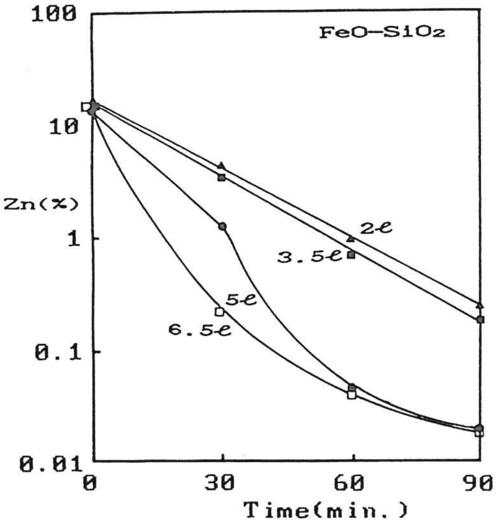

Fig.5. Change of zinc in silicate slag with gas rate at 1523 K.

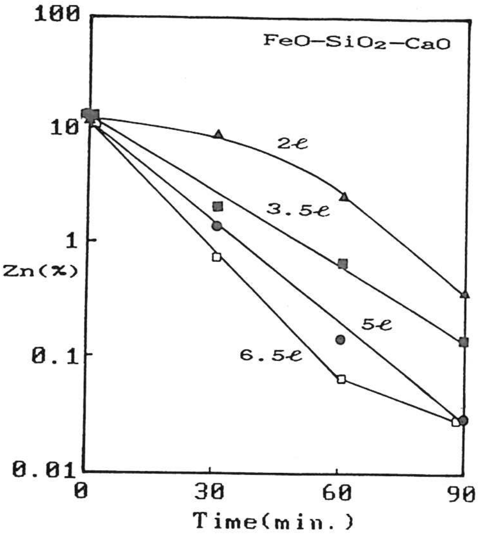

Fig.6. Change of zinc in calcium-silicate slag with gas rate at 1523 K.

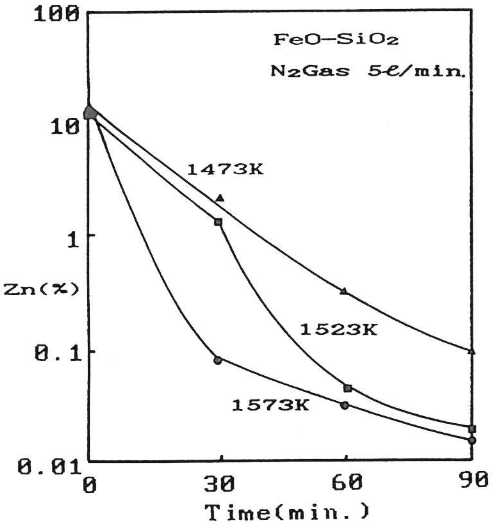

Fig.7. Change of zinc in silicate slag as a function of temperature.

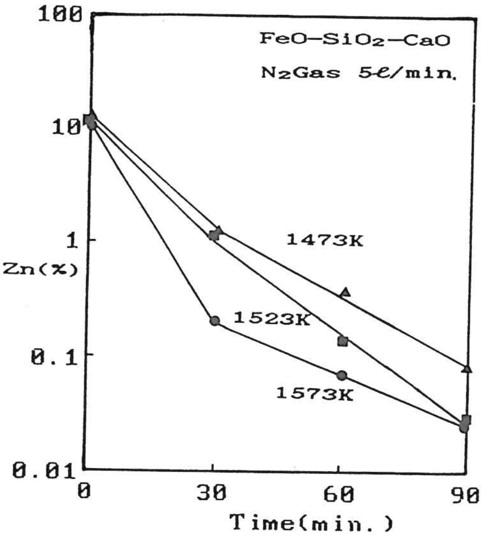

Fig.8. Change of zinc in calcium-silicate slag as a function of temperature.

increased. Fig.9 shows the change of Zn and Fe^{3+} in slags with carbon content. As carbon content increased Zn and Fe^{3+} in final silicate slag decreased. But in final calcium-silicate slag, those were nearly constant.

Eqns. (11), (12), (13) were derived from eqn. (6) using $\Delta G^o = -RT \ln K$.

$$\ln \frac{P_{Zn} \cdot P_{CO_2}}{a_{ZnO} \cdot P_{CO}} = \frac{-21411}{T} + 13.43$$

$$\text{Log } P_{O_2}\ (\text{atm}) = 2\log(P_{CO_2}/P_{CO}) - 29510 / t + 9.05\ (12) \tag{12}$$

$$\log P_{Zn} = -9740 / T + 6.12 - \log(P_{CO_2}/P_{CO}) + \log a_{ZnO} \tag{13}$$

Where a_{ZnO} (8) was used 2.15 in $FeO-Fe_2O_3-SiO_2-ZnO$ slag. The log P_{O_2} was calculated from log $(N_{Fe^{3+}}/N_{Fe^{2+}})$ (7),(14) value obtained during experiment. And the real partial pressure of zinc, $*P_{Zn}$(11) was obtained from the weight loss of ZnO(W) and the volume of gas(Vo) for standard temperature and pressure. It is given by following equation.

$$*P_{Zn} = 22.4\ W / 81.37\ Vo \tag{14}$$

The real partial pressure($*P_{Zn}$) is equal to average value of P_{Zn} with time(min).

The obtained v alues of P_{Zn} and $*P_{Zn}$ are listed in Table 3 with gas injection time.

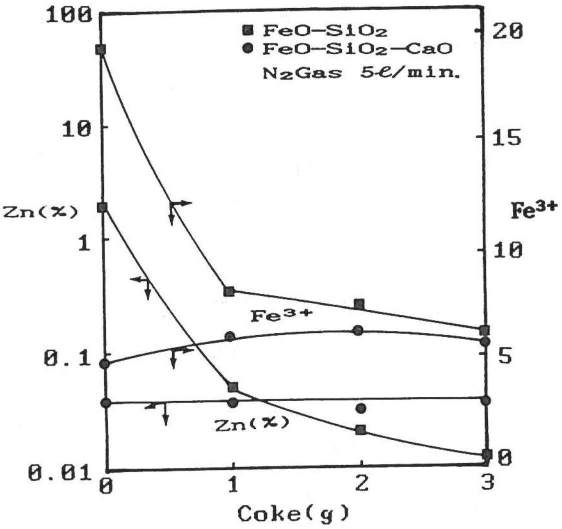

Fig.9. Change of zinc and Fe^{3+} in slag as a function of coke contet at 1523 K.

Table 3. The relation of P_{O_2}. P_{Zn}.$*P_{Zn}$ with gas injection time at 1523 K and $FeO-SiO_2$ slag.

atm Time	0	15	30	45	60	75	90
P_{O_2}	4.0×10^{-9}	4.2×10^{-8}	3.3×10^{-8}	2.1×10^{-8}	2.3×10^{-8}	1.7×10^{-8}	3.0×10^{-9}
P_{Zn}	2.2×10^{-2}	4.6×10^{-3}	4.4×10^{-3}	9.8×10^{-4}	2.5×10^{-4}	5.9×10^{-5}	4.1×10^{-5}
$*P_{Zn}$		5.3×10^{-2}	6.5×10^{-3}	2.0×10^{-4}	8.4×10^{-4}	2.8×10^{-4}	1.81×10^{-5}

4. CONCLUSION

The method of submerged injection smelting process was done to eliminate Zn and Pb from Steel-Dust with vaporization

1. The contents of Zn and Pb in silicate slag and calcium-silicate slag decreased rapidly for 30 minutes after gas injection.
2. In the present study, the vapor pressure of Zn agrees well to the calculated value by below equations.

$$\text{Log } P_{Zn} = -9740 / T + 6.12 - \log(P_{CO_2}/P_{CO}) + \log a_{ZnO}$$

$$*P_{Zn} = 22.4\ W / 81.37\ Vo$$

3. The vaporization rates of Zn and Pb increased rapidly in the initial stage of gas injection due to the large ferrous-ferric ratio.

ACKNOWLEDGMENTS

The authors wish to thank personnel of the Korea Zinc Co. for their valuable advice and chemical analysis and this study was done with the research fund of Pohang iron and steel company on 1991.

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