

1. Introduction

In an electric furnace, which is a method of a steel manufacturing process that mainly uses scraps including zinc-coated steel plates, about 400,000 tons of dust is generated per year in Japan, and about 8,000,000 tons of dust is generated per year around the world. In recent years, the production amount of zinc-coated steel plates is increasing in response to the market demands for rust-proofing. As a result, scraps of zinc-coated steel plates are increasing. Therefore, the dust generated in electric furnaces contains 20% to 35% of zinc in a form of oxide. The most part of the zinc is separated from iron and extracted as crude zinc oxide by dust collection companies, and then refined to be metallic zinc by zinc refineries. In this document, we report that we have developed a recovery process of zinc to metallic zinc and carburizer that can achieve remarkably high economic rationality in one process and three steps by using the selective chlorination method.

2. Summary of process

(1) Conventional technique

At present, electric furnace dust is processed by the Waelz Kiln method or the like, and crude zinc oxide containing a large amount of impurities is collected and processed by zinc refineries, and the residues (clinkers) are disposed by landfill as industrial waste. In this carbon reduction step, zinc oxide in electric furnace dust is once subjected to carbon reduction. However, after evaporation it is oxidized again, and is eventually recovered as crude zinc oxide having approximately 60% of Zn content. The recovered crude zinc oxide is subsequently refined to be metallic zinc by zinc refineries.

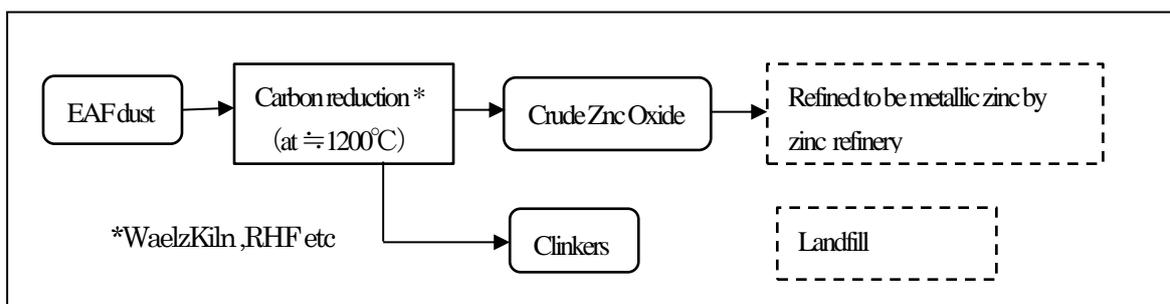


FIG. 1 Electric furnace dust treatment process using conventional technique

(2) Present process by selective chlorination method

According to this method, by using the selective chlorination method, iron in iron oxide (Fe_2O_3) and zinc ferrite (iron zinc oxide: ZnFe_2O_4) in electric furnace dust is remained as iron oxide, and only zinc is chlorinated. Due to this process, zinc chloride can be recovered as metallic zinc by electrolysis in the subsequent process. Meanwhile, iron oxide in the dust remaining in the residues of the chlorination step can be returned through a reduction step to a steel manufacturing process (electric furnaces or the like) as carburizer.

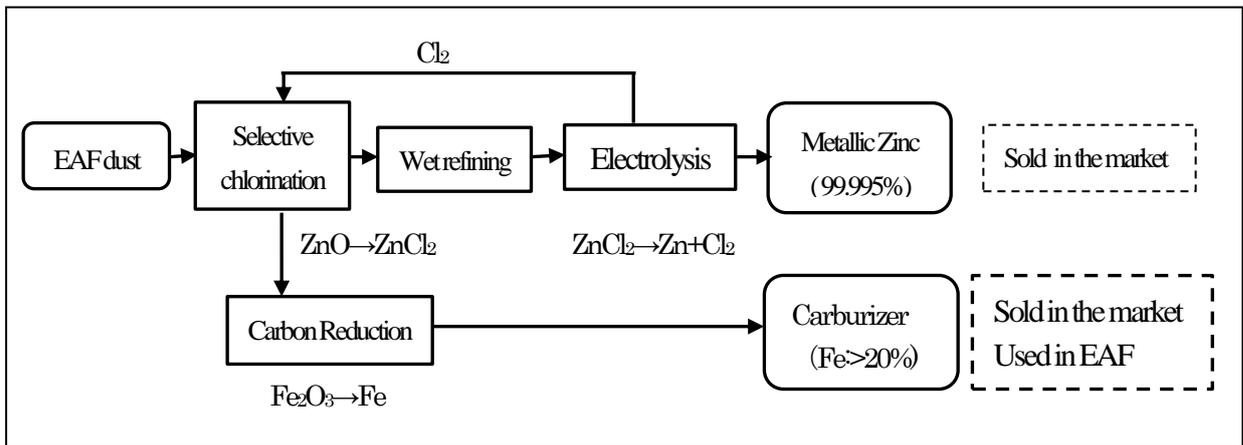
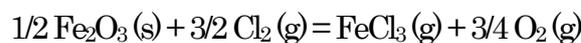


FIG. 2 Electric furnace dust treatment process using selective chlorination method (Kinotech method)

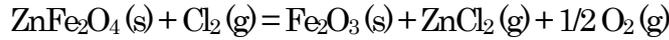
3. Progress on experiments

(1) Principle of selective chlorination

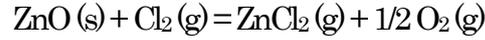
Chlorination reaction of respective oxides near a temperature of 1023 K has been considered as follows. That is, based on the standard Gibbs energy change for chlorination reaction, chlorination reaction of zinc and lead tends to occur around a temperature of 1023 K, while iron chloride is hard to form under a standard condition.



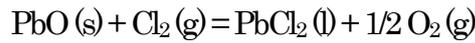
$$\Delta G^\circ = 144100 - 98.91 T \text{ [J/mol]} \quad (1)$$



$$\Delta G^\circ = 88500 - 91.43 T \text{ [J/mol]} \quad (2)$$



$$\Delta G^\circ = 73840 - 100.6 T \text{ [J/mol]} \quad (3)$$



$$\Delta G^\circ = -139500 + 274 T - 34.2 T \ln T \text{ [J/mol]} \quad (4)$$

By controlling the partial pressure of air and chlorine in the hatched area in FIG. 3, chlorination of iron oxide contained in the dust is suppressed, and chlorination of zinc oxide can be progressed selectively. Due to this process, by reducing the iron oxide to metallic iron without oxidizing it, the iron oxide can be returned to a steel manufacturing process (electric furnaces). Further, the load in a refining step in the subsequent process can be decreased. Based on this principle, chlorination step operating conditions are decided and electric furnace dust is separated into crude zinc chloride and residues.

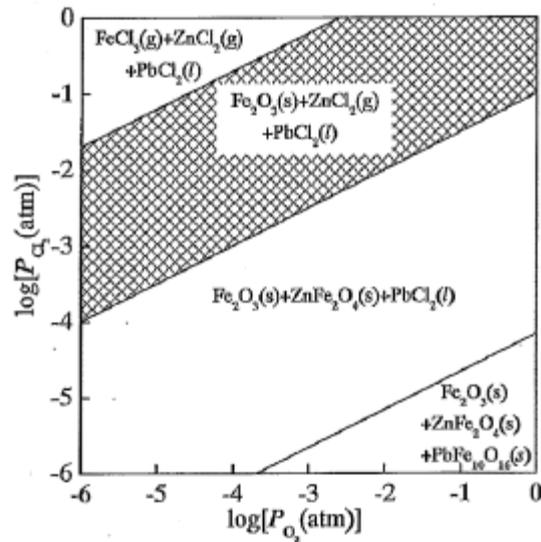


FIG. 3 Fe-Zn-Pb-O-Cl potential diagram in 1073 K (by Hiroyuki Matsuura, Associate professor, the University of Tokyo)

(2) Chlorination

It has been studied to use a fluidized bed in a commercial furnace, and experiments are under way on a batch-type fluidized bed in the laboratory. Electric furnace dust is put into a reactor vessel, chlorine gas is filled into the reactor vessel with preheated air to let them flow in the reactor vessel. At this time, chlorine and air are maintained at a ratio of 1:9, and a tubular furnace is maintained at a temperature of 800°C (1073 K). Gasified zinc chloride is cooled and recovered as a solid, and the residues (that is, residual dust) are collected by glass wool. While this method uses a batch furnace, production of a continuous fluidized bed where supply of dust is continuously performed is currently under way.

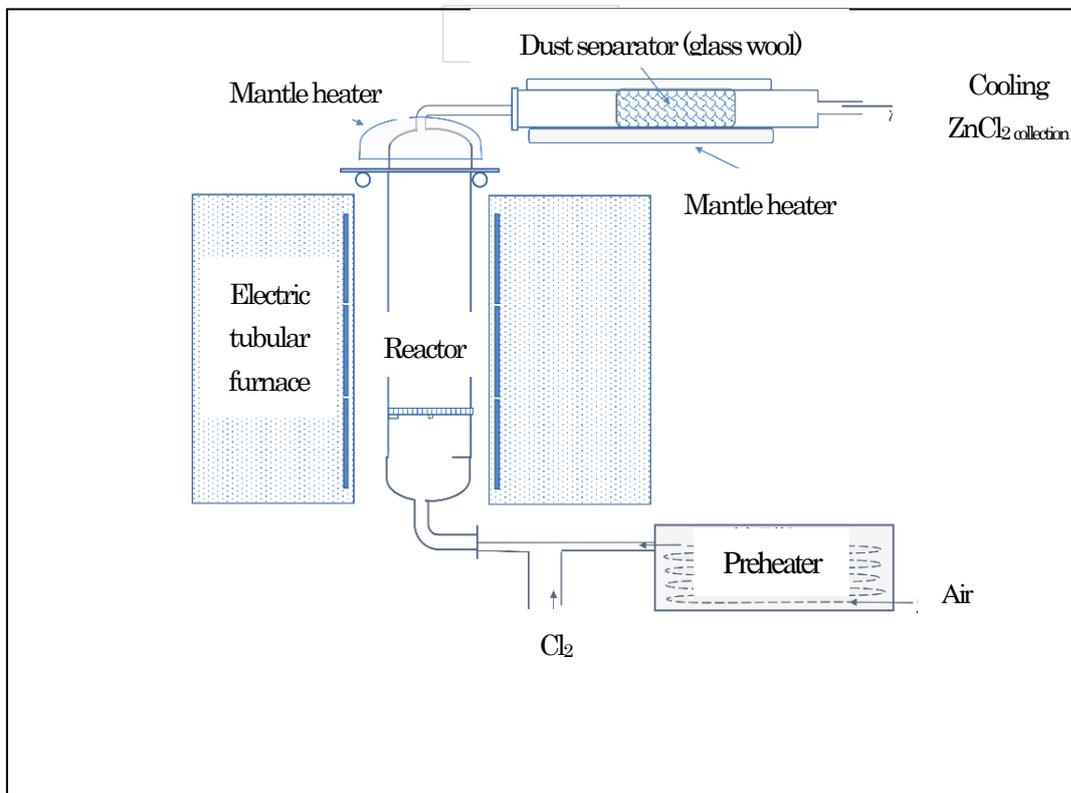


FIG. 4 Fluidized bed experiment device

(3) Wet refining

Crude zinc chloride obtained in a chlorination step includes impurities such as iron chloride and lead chloride of less than 1%, although having undergone selective chlorination. In order to obtain high purity metallic zinc, refining needs to be performed at the stage of where it is still crude zinc chloride. Initially, experiments were conducted to refine and separate zinc chloride

by using boiling point differences. However, handling of molten zinc chloride is difficult, and it may hinder stable continuous operation. Therefore, it was decided to perform refining with a wet refining method with which industrialization is simpler.

The wet refining uses crude zinc chloride in a form of aqueous solution, and refined zinc chloride is obtained by sequentially adding chemicals to precipitate the crude zinc chloride and then filtering the precipitation.

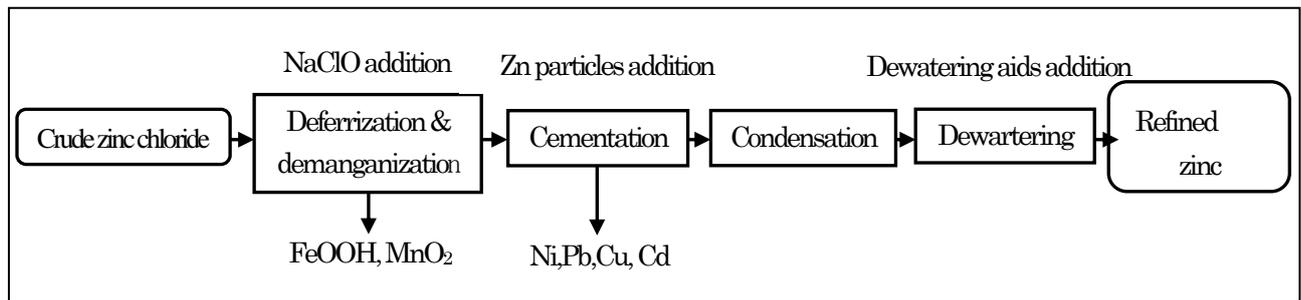


FIG. 5 Wet refining experiment

Table 1. Analysis value of wet refining samples

	Aqueous solution of crude zinc chloride [mg/l]	Filtrate of deferrization-demanganization [mg/l]	Refined zinc chloride [wt%]
Na	< 4700	6512	4.1
Mg	3	1	0.0019
Al	< 300	< 30	< 0.002
K	< 6700	< 700	0.28
Ca	21	3	0.0053
Cr	< 70	< 10	< 0.0004
Mn	200	< 3	< 0.0001
Fe	480	< 3	< 0.0001
Ni	< 80	< 8	< 0.0005
Cu	< 460	< 50	< 0.003
Cd	98	73	< 0.0004
Sn	< 290	95	< 0.02
Pb	< 410	< 40	< 0.003

Zn	77900	60420	41.6
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(4) Electrolysis

Electrolysis experiments were conducted by using refined zinc chloride, which was obtained by performing selective chlorination and wet refining with respect to electric furnace dust. Stable electrolysis was performed under current conditions of a temperature of 550°C and a current density of 0.55 A/cm² at an electrolysis voltage of about 13 V. This electrolysis voltage includes a voltage drop of about 10 V caused by a graphite electrode bar.

34 grams of metallic zinc was recovered from 540 grams of refined zinc chloride. The ratio with respect to a theoretical electrolytic zinc amount (current efficiency) was 67.0%, the decomposition voltage was 1.4 V, and the solution resistance was 5 Ωcm.

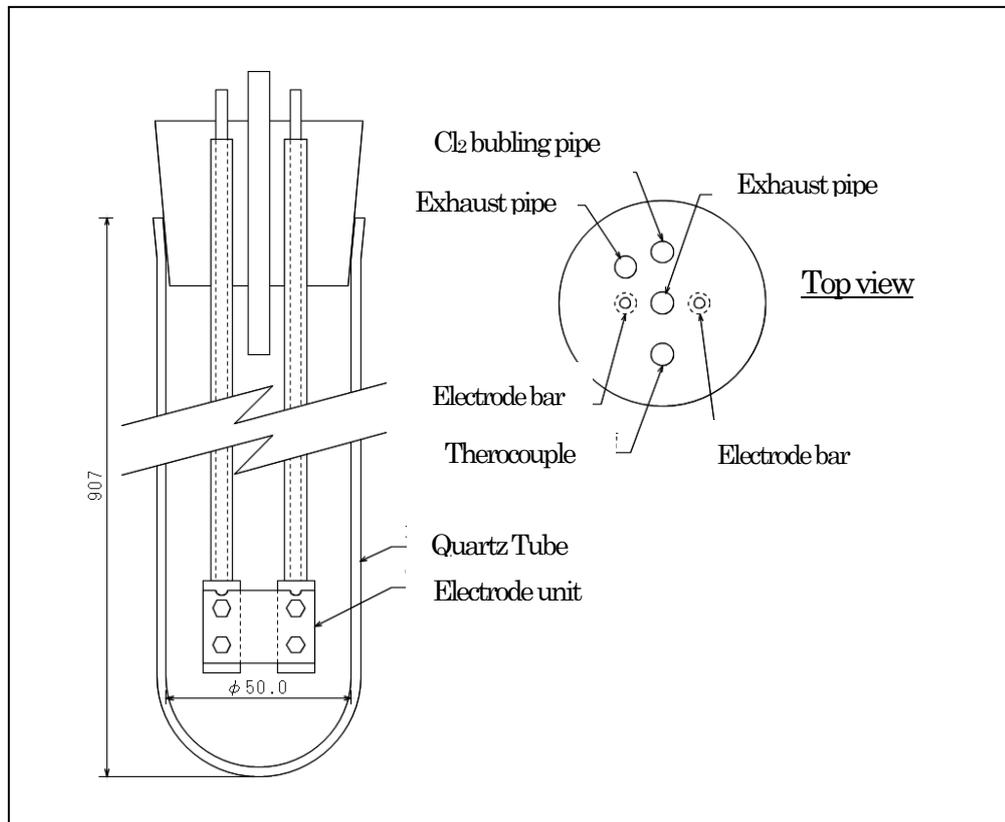


FIG. 6 Electrolysis experiment device



FIG. 7 High purity metallic zinc obtained by electrolysis

(5) Transition of chemical components

Transition of chemical components in the above process is summarized in Table 2. The chemical component value of metallic zinc recovered in this process satisfies the IME grade specified by ASTM B6.

Table 2 Chemical analysis values from dust to metallic zinc [mass%]

Element	Dust ^{*1)} (mainly oxide)	Crude zinc chloride ^{*2)} (mainly chloride)	Wet-refined zinc chloride ^{*3)} (mainly chloride)	Metallic zinc ^{*4)} (mainly solid solution element)	LME Grad (ASTM B6-13)
Zn	31.8	49.6	41.6	99.995	99.995
Al	0.37	-	< 0.002	< 0.0002	0.001 max
Mn	1.51	0.02	< 0.0001	< 0.0001	-
Fe	22.2	0.05	< 0.0001	0.0012	0.002 max
Cu	0.21	0.07	< 0.003	< 0.0003	0.001 max
Cd	0.11	0.10	< 0.0004	0.0002	0.003 max
Sn	0.05	-	< 0.02	< 0.002	0.001 max
Pb	1.44	0.26	< 0.003	< 0.002	0.003 max
Remnant	Oxygen	Chlorine	≐ 0	≐ 0	Total non zinc 0.005max

Analysis method: *1) Fluorescent X-rays, *2), *3), *4) ICP

(6) Metalli

c iron recovery from residues

Experiments were conducted to obtain metallic iron from iron oxide remaining in residues by carbon reduction and to effectively use the obtained metallic iron, which is an advantage of selective chlorination.

When residues after carbon reduction were analyzed by XRD, a strong peak of Fe was confirmed, and it was confirmed that the iron oxide was reduced to metallic iron. A predetermined amount of carbon was added after the carbon reduction so as to realize sales to the market as recarburizer (used in electric furnaces). As for the evaluation as carburizer, as well as evaluations obtained by using the XRD method described above, such results were obtained as grounds for the quality as recarburizer that all metallic iron in the quantity of the residues of carbon reduction determined by a bromine methanol method (ISO 5416) and carbon (recarburizer) was 52%, and the quantity of oxygen by the LECO method being 28.6% in a sample before reduction was decreased to 16% after reduction.

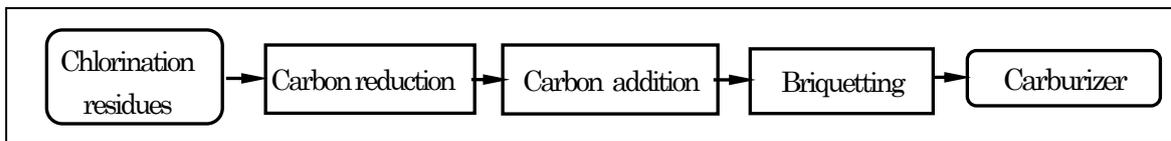


FIG. 8 Carburizer manufacturing process based on experiment results

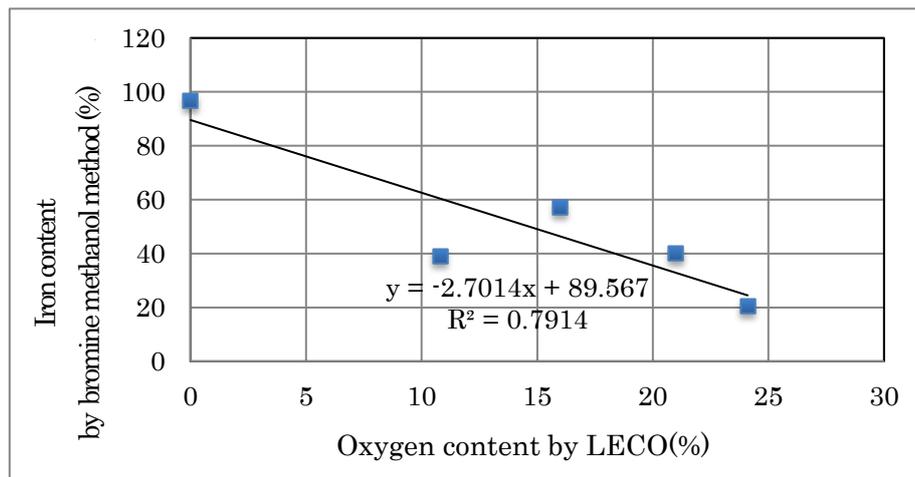


FIG. 9 Relation between oxygen analysis value after carbon reduction of residues and iron value obtained by bromine methanol method

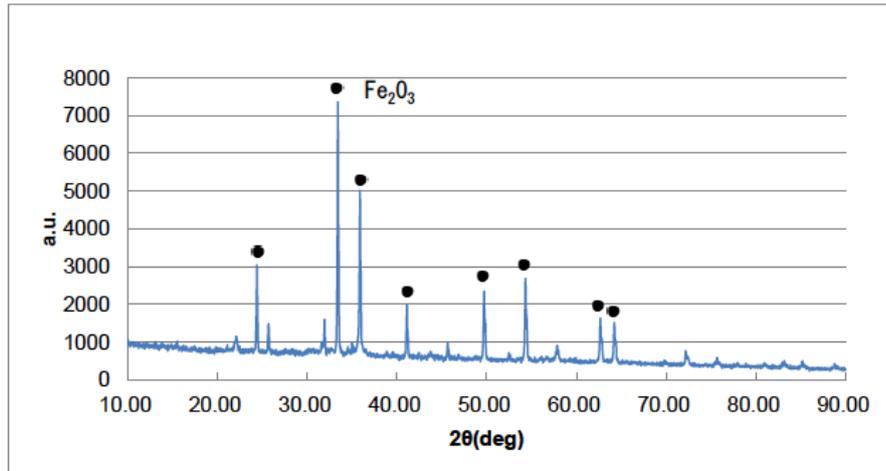


FIG. 10 XRD spectrum of residues before carbon reduction

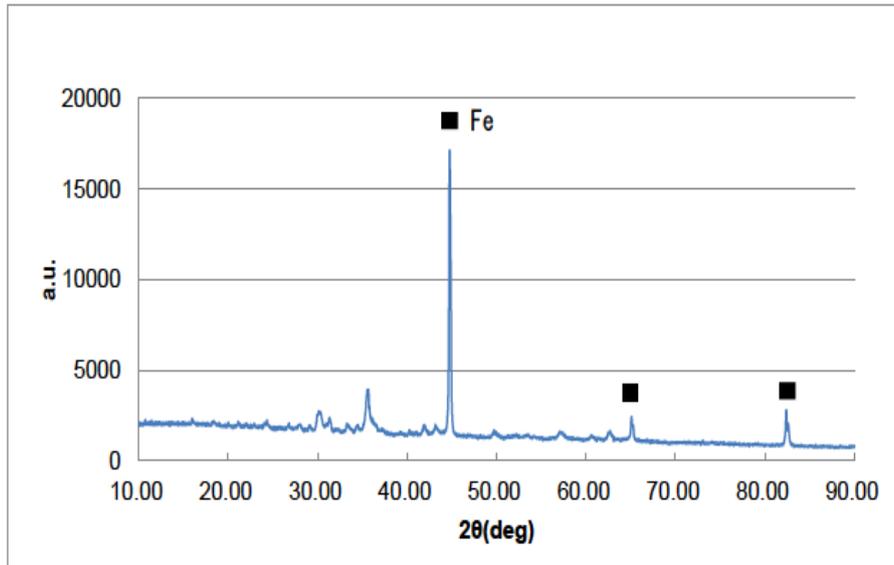


FIG. 11 XRD spectrum of residues after carbon reduction

4. Conclusion

In summary, it was confirmed that, as shown in Table 3, it was possible to effectively recycle valuable resources in electric furnace dust by separating zinc and iron in electric furnace dust into metallic zinc and residues.

Table 3 Transition of zinc and iron from electric furnace dust [mass%]

	Electric furnace dust	Purified zinc chloride	Electrolytic metallic zinc	Residues
Zn	31.8	41.6	99.9987	0.24
Fe	22.2	<0.0001	0.0012	43.4

5. Future developments

It was confirmed that high purity zinc was obtained in a consistent process from selective chlorination to electrolysis in the laboratory. From the next fiscal year, with the prospect of actual plant, calculation of plant construction cost, studies on manufacturing cost, and studies on plant operation conditions will be made.

Year 2018 to 2020: Demonstration experiments and designing of pilot plant

Year 2021 onward: Operation of pilot plant

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