

Properties of Zinc and Lead Hydroxyl Chloride in EAF Dust

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ABSTRACT

The electric arc furnace (EAF) dust used in this experiment showed the formation of an irregular agglomerate of small spherical particles and consisted of 27.5% Fe, 18% Zn, 4.83% Pb and 10.2% CaO, and it also contained 3.26% Cl and 0.15% F. IR spectra peaks of Pb(OH)Cl were observed at 1630 and 1377 cm^{-1} regions and the intensity decreased using an acid treatment (1N H_2SO_4) and thermal treatment at above 600°C, but it was not affected by washing process. Those of $\text{Zn}_3(\text{OH})_2\text{Cl}_2$ treated by oxidation showed broad absorption peak at 3600~3200 cm^{-1} , main peaks at 1136 and 1040 cm^{-1} and a splitting peak at 991 and 921 cm^{-1} which were believed to be due to ZnO by oxidation at about 700°C. The IR spectra of the dust residues by a washing process show the same peaks at 3449, 1635, 1439, 875, 571 and 455 cm^{-1} regions, but the peaks at 2942, 2862, 1136 and 1040 cm^{-1} decreased and disappeared using an acid treatment and washing process, which is believed to be due to the dissolution of zinc hydroxyl chloride.

1. Introduction

Much of metallurgical wastes from various smelting plants in Korea contain high levels of zinc, copper and lead, etc. These wastes could be converted into high-value products if suitable recovery processes were employed. Currently, there are several stockpiles of such waste materials which have been accumulated over the past decade, awaiting a proper technology to process them.

Typically, electric arc furnace (EAF) dust which is generated in Korea contains 20~25% Zn, 5~6% Pb and 1~5% Cl, whereas basic oxygen furnace (BOF) dust contains 2~8% Zn, 0.2~1% Pb and 50~80% Fe. EAF dust could be an important source of nonferrous metal. The amount of dust and its chemical composition depend on the adopted process of steelmaking and source materials. Therefore, the reduction apparatus and processing methods of zinc and lead, the refining of the reduced zinc and lead, and removal of chloride are very important for the practical use of EAF dust.^{3,9} Chloride is usually condensed with zinc and lead metals to easily form metal hydroxyl chloride. Also, it can cause a decrease in the refining process recovery rate at the electrolytic dissociation.⁹

A recent review of the coupling and band structure of chloride in dust by Li and Tsai⁹ has reported that zinc hydroxyl chloride is generated by the thermal dissolution of zinc oxide and hydrochloric acid from a polyvinyl chloride

substance. Noguchi *et al.*⁷ have detailed the coupling and reaction of chlorine from sodium chloride and lead hydroxyl chloride existing in dust.

The properties of dust residues treated using an i) oxidation thermal treatment, ii) an acid treatment and iii) a washing process were tested to investigate the behavior of thermal solubility in acid solution and aqueous solution for the hydrometallurgical and pyrometallurgical processing of EAF dust.

2. Experimental Procedure

The electric arc furnace dust used in this experiment was taken from the dust container of a steelmaking plant, KW Ins. Co., in Korea. The sample for every test was taken using the following standard sampling procedures as to ensure its representation. The mineral composition and chemical analysis were examined by SEM/EDX (JEOL Co., JSM-5400) and XRF (Simens Co., SRS-303), and the crystal phase was identified by X-ray diffraction (X-ray diffractometer, Rigaku Co., D/Max-1200) using Cu K α radiation. IR spectra of the compounds were obtained by FT-IR Spectrometer (Nicolet Ins., Co., 520P) using the standard KBr disc. A thermal analysis with 20 mg of the sample and a heating rate of 10°C min^{-1} in air was carried out by TG-DTA (Mac Science Co.).

These samples were made using the following three types of experimental procedures to investigate the behavior of metal hydroxyl chloride in dust.

i) To verify the thermodynamic properties of dust, laboratory tests were carried out using a tube furnace. The samples were roasted in the oxidizing isothermal zone in an alumina boat at a constant air flowrate of 200–500 cc/min and various roasting temperatures from 200 to 1100°C for 60 mins. respectively.

ii) To examine the effects of acid treatment, distilled water and reagent grade H₂SO₄ were used to prepare the leaching solution. 10 g of the sample was leached under the condition of 1/10 of solid/liquid mass ratio with 100 ml liquid, 60 min. of leaching time and 300 r.p.m. of stirring speed. Leached residues were filtered and dried for analysis.

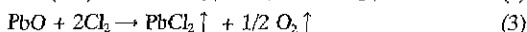
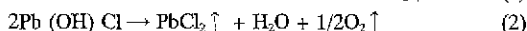
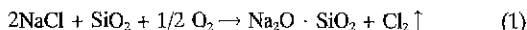
iii) To test the solubility of metal hydroxyl chloride, a washing process method was adopted in 100 ml aqueous solution with 10 g sample for 120 mins. agitation with 200 r.p.m., and then residue was analyzed.

3. Results and Discussion

3.1. Component and composition

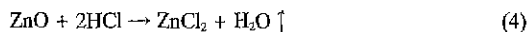
The original sample of dust was analyzed chemically and the results are listed in Table 1. It shows that the dust consisted of 27.5% Fe, 18% Zn, 4.83% Pb and 10.2% CaO. It also contained 3.26% Cl and 0.15% F, which strongly influenced the hydrometallurgical and pyrometallurgical processes. Especially, it was very important to study the behavior of chloride in the reduction process of dust because it reacted together with Zn and Pb as ZnCl₂ and PbCl₂ etc.

Neguchi *et al.*⁷⁾ reported that chlorides such as NaCl and Pb(OH)Cl can be removed completely (100%) by a thermal treating method in air at about 1000°C, and also that the reactions of oxidation (Eqs. 1 and 2) and chlorination (Eq. 3) promoted the evaporation of Pb at high temperatures.



On the other hand, ZnCl₂ generated by the reaction

between ZnO and HCl (Eq. 4). In this case, HCl was produced by the thermal reaction of polyvinyl chloride materials.^{6,8)}



Therefore, in order to investigate the behavior and existence of chloride in dust residues the sample was tested by IR, XRD and SEM/EDX.

Fig. 1 shows the X-ray diffraction patterns of the sample. The strong peaks of zinc ferrite and zinc oxide are major phases, and the weaker peaks of lead hydroxyl chloride and sodium chloride were observed. These results were in strong agreement with the results of numerous investigators.^{9,10)} The XRD patterns of zinc hydroxyl chloride as Zn₃(OH)₈Cl₂ were not observed. The absence of Zn₃(OH)₈Cl₂ and Zn₃(OH)₈Cl₂ · H₂O peaks in these XRD patterns may not indicate the absence of zinc hydroxyl chloride in dust. It might be present in such a small amount that it can not be detected. Therefore, IR spectra analyses were carried out to verify the existence of zinc hydroxyl chloride in dust. Hwang *et al.*⁹⁾ and Li and Tsai¹⁰⁾ reported that the spherical particles of EAF dust were composed of ZnFe₂O₄ and ZnO, and they were analysed using SEM/EDX. The results are shown in Fig. 2. The small spherical particles were formed of irregular agglomerates due to the melting nature of ZnCl₂¹¹⁾ which played a binding role between ZnFe₂O₄ and ZnO to form Zn₃(OH)₈Cl₂ · H₂O.⁶⁾ But the formation of irregular agglomerates is easily separated into ZnFe₂O₄ and ZnO by acid treatment, thermal treatment, and a washing process. The major components of spherical

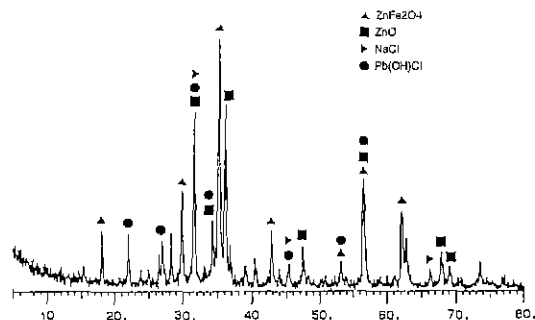


Fig. 1. X-ray diffraction patterns of the sample.

Table 1. Chemical analysis of the dust sample used

	T.Zn	T.Fe	M.Fe	Pb	Cu	Cr	Cd	Mn	Ni	Na ₂ O	SiO ₂	CaO	MgO	Al ₂ O ₃	C	Cl	F	T.S	Ig.loss
Ass.(%)	18.0	27.5	7.16	4.83	0.29	0.21	0.33	1.57	0.03	2.66	3.86	10.2	4.55	1.16	1.22	3.26	0.15	0.58	12.44

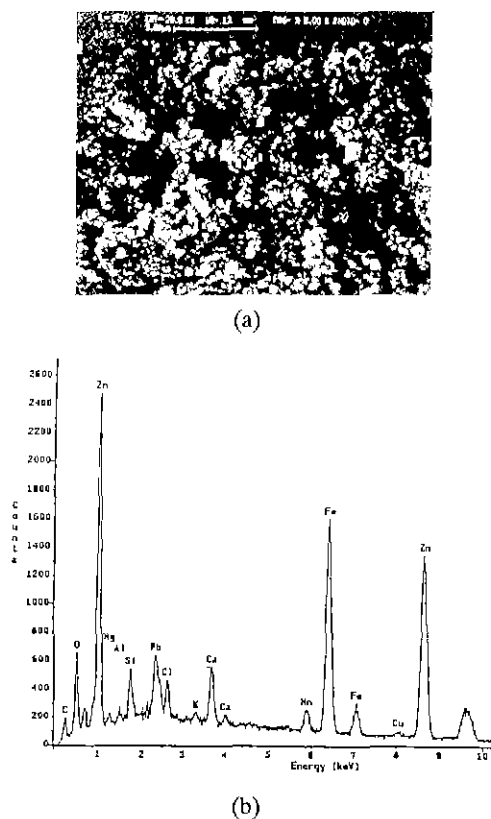
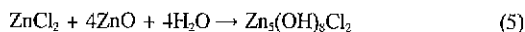


Fig. 2. SEM micrograph (a) and EDX (b) analysis of the sample

particles were Zn, Mn, Fe, Ca, Pb and Cl ions.

Fig. 3 shows the results of IR spectra of a raw dust sample, and the references of metal hydroxyl compounds from Srivastava and Secco¹²⁾ are shown in Table 2 to compare the results. Generally, IR spectra of sodium chloride show a plate type at 3,800~4000 cm^{-1} , and IR spectra of $\text{Pb}(\text{OH})\text{Cl}$ occur in the 1504 to 1370 cm^{-1} region with strong distinct doublets.¹³⁾ Therefore, the combination of Cl existing in dust could be inferred from the lead or zinc hydroxyl chloride better than sodium chloride from IR spectra.

In the dust generating process, $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ was produced as following Eq. 5 and metal hydroxyl compounds such as $\epsilon\text{-Zn}(\text{OH})_2$, $\beta\text{-ZnOHCl}$, $\text{Zn}_5(\text{OH})_8\text{Cl}_2$, ZnOHF , $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Pb}(\text{OH})\text{Cl}$, which could occur simultaneously.



The bands occurring in the 3600~3260 cm^{-1} region are generally attributed to the fundamental OH stretching mode. The band with a peak frequency at the 3416 cm^{-1} region in dust agrees with 3480 cm^{-1} in $\beta\text{-ZnOHCl}$, $\text{Zn}_5(\text{OH})_8\text{Cl}_2$, and Zn_5

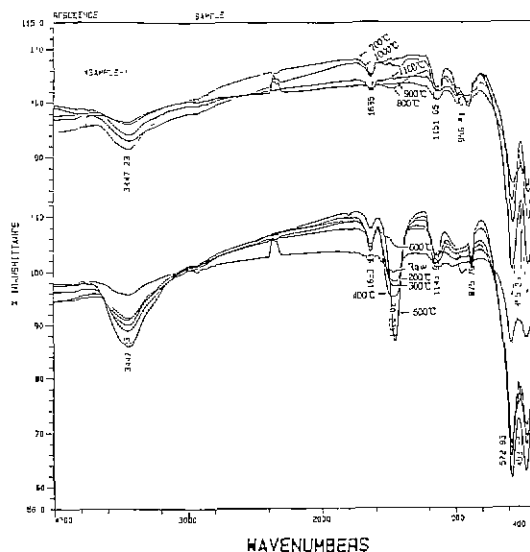


Fig. 3. Infrared spectra of dust treated at various temperature.

$(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, already reported by Glemser and Hartert.¹⁴⁾ From $\text{Zn}(\text{OH})_2$ to $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ in the sequence, as shown in Table 2, the band became sharper, accompanied by a splitting in ZnOHF and $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ with the peak frequency shifting to higher values. The distinct doublet at 3590 and 3400 cm^{-1} in ZnOHF was most likely affected by a strong intermolecular coupling of the OH stretching vibration of the molecules in the unit cell.¹²⁾ However, the distinct doublet band at above 3400 cm^{-1} in dust was not observed. This strong coupling was expected to give rise to splitting in other bands involving OH such as ZnOH banding and OH twisting vibrations, which are observed in the 755~1015 cm^{-1} region for the metal hydroxyl compounds. However, the 3400 cm^{-1} band could have arisen from a different combination band involving a lattice vibration of 1900 cm^{-1} and the fundamental at 3590 cm^{-1} .

The free-hydroxyl stretching vibration is distinguishable from the O-H stretching vibration in water by the reduced frequency and increased broadening of the latter. In the case of water hydration, there was less chance of a hydrogen-bonding effect, and thus vibrational stretching and banding were observed in region 3600~3200 cm^{-1} region and near 1650 cm^{-1} , respectively. In the case of raw dust, the vibrational stretching and banding appeared, respectively, as a single broad absorption band in the 3500~3200 cm^{-1} region, and as a weak absorption in the 1650~1600 cm^{-1} region.¹⁵⁾ Therefore, the presence of lead hy-

Table 2. Infrared absorption band wave numbers of dust and zinc hydroxyl compounds

Dust sample	ϵ -Zn(OH) ₂	β -ZnOHCl	ZnOHF	Zn ₅ (OH) ₈ Cl ₂ · H ₂ O	Zn ₅ (OH) ₈ Cl ₂
	-	-	-		3600(vs) 3590
	-	-	3590(vs)	3520(vs)	
	-	-	-	-	3540(vs) 3480
3416(w)	3260(vs)	3480(vs)	3480(vs)	3490(vs)	
2942(w)	-	-	-	-	
2862(w)	-	-	-	-	2930 2870(vw) 2330
-	-	-	-	-	
1643(v)					
1464(v)					
	1080				
1136(m)				1015(m)	1030(w) 990(m)
	1025				
1040(w)					
875(w)	-	850(vs)	855(m)	895(vs)	870(vs)
	830(w)	830(w)	-	-	815(s)
	-	790(vs)	780(vs)	-	
	750(w)	755(vs)	-	-	695(vs)
572(vs)	715(s)	-	-	715(vs)	
459(vs)					

Table 3. Infrared absorption band wave numbers of dust treated various conditions.

Raw dust	Temperature (°C)										Acid treatment (1N H ₂ SO ₄)	Washing by water	
	200	300	400	500	600	700	800	900	1000	1100		Sink residues	Float residues
3416	3477	3441	3447	3449	3437	3443	3422	3429	3429	3437	3439	3449	3453
2942	-	-	-	-	-	-	-	-	-	-	-	-	-
2862	-	-	-	-	-	-	-	-	-	-	-	-	-
1643	1633	1635	1631	1633	1635	1635	1643(w)	1643(w)	1639(m)	1635(m)	1635	1635	1631
1464	1486	1446	1448	1444	1423	1423(w)	(vw)	-	-	-	VW	1439(vs)	1452(vs)
1136	1143(m)	W	W	1163(m)	1147	1147	1147	1149	1142	1142(w)	-	-	-
											1026	-	-
1040	VW			VW	949	921	921	921	921	921	900(m)	-	-
875	W	875	875	877	-	-	-	-	-	-	-	875(m)	875
572	572	572	571	569	567	569	569	571	571	565	572	571	571
459	453	459	455	459	457	455	451	453	449	430	445	455	445

droxyl chloride as seen in the results of IR spectra in Table 3 was confirmed by the broad absorption peak in the 3600-3200 cm⁻¹ region and the weak band at 1643 cm⁻¹ which was not reduced but increased by the OH

stretching vibration at about 600°C. Also, the IR absorption bands at 1040 and 875 cm⁻¹ showed a low frequency, and these bands were splitting to 991 and 921cm⁻¹ which were regarded, as ZnO⁶ at about 700°C.

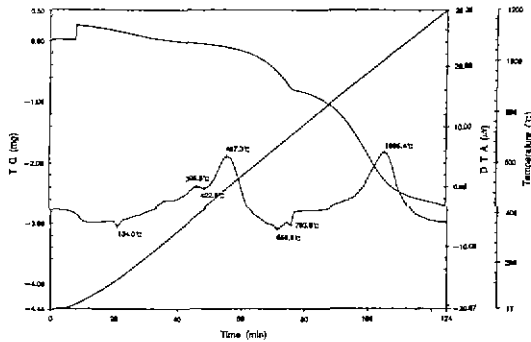


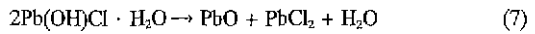
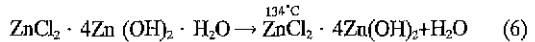
Fig. 4. TG-DTA thermogram of dust sample

3.2. Oxidation reaction of metal hydroxyl chloride in dust

Fig. 4 shows the results of DTA-TG to investigate the thermal properties of dust. At the reaction temperature scan of 10°C/min., endothermic peaks were observed at 134, 422, 659 and 703°C, while exothermic peaks were observed at 497 and 1006°C. The results of DTA reported by Srivastava and Secco¹⁶⁾, for $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ and $ZnCl_2 \cdot 4Zn(OH)_2$ showed the endothermic peaks at 127, 187 and 200°C, and these peaks at 127°C denote the dehydration of $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$. Also Li and Tsai⁶⁾ reported that the endothermic peaks shown at 127, 187, 210 and 262°C, and a secondary endothermic peak as a weak peak at 262°C were explained as a $ZnCl_2$ melting process, and the endothermic peak at 708°C was due to the vaporization of li-

quid $ZnCl_2$.

In the case of this dust sample, the endothermic peak from DTA-TG analysis shows a single peak at 134°C as following Eqs. 6 and 7. This result corresponds to the disappeared peaks of dust treated at 200°C from the results of IR spectra at 2942 and 2862 cm^{-1} in Table 3. But the endothermic peak at 290°C, which can be explained by the melting point of $ZnCl_2$, was not present in this dust.



The peaks at 395-497°C were considered as exothermic peaks when the organic matter and carbon (1.22%) were burning and lead oxide converted slowly into Pb_3O_4 , but at higher temperatures it reverted to a lead chloride reaction.¹⁷⁾ This result corresponded to the result of IR spectra at the 1464 cm^{-1} region. The strong peak was observed by a OH stretching vibration at under 600°C. But when the heating temperature was increased to above 600°C, it decreased at 600°C due to the reactions followed by Eq. 2 and 3.

Fig. 5 shows the volatilization rates of Pb, Cl and Zn in dust under oxidation atmosphere. The evaporation ratio of 25% Pb and 35% Cl_2 , respectively were observed at 800°C, and each of them was above 95% at 1050°C. Namely, $PbCl_2$ was decomposed at about 500°C and mostly removed at 1100°C, the exothermic peak at 1006°C was considered as the chlorization of PbO as in Eq. 3 and the reduction of iron oxide and other metals. Otherwise, Cl_2 and PbO which did not react under the above conditions, reacted with SiO_2 to form silicate substances with a low fusing point, and these substances must be affected to prevent the evaporation

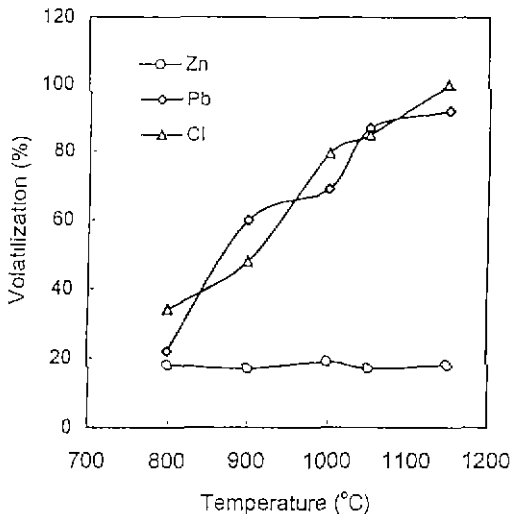


Fig. 5. The volatilization rates of Pb, Cl and Zn in dust under oxidation atmosphere.

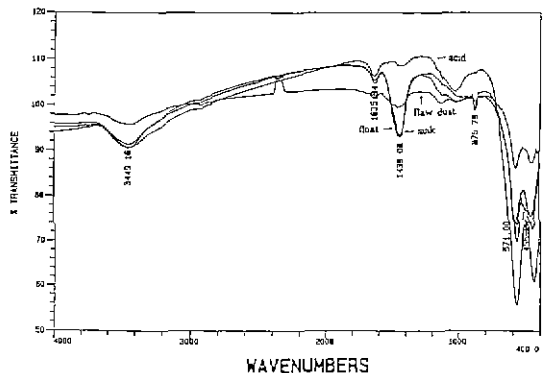


Fig. 6. Infrared spectra of dust treated by acid and washing process.

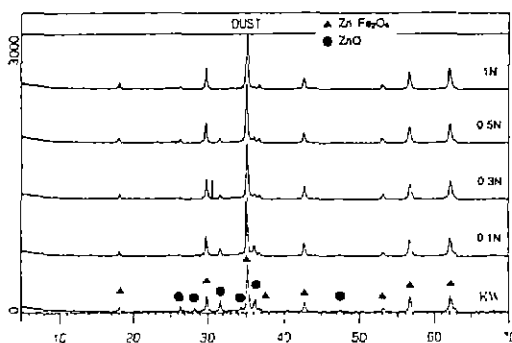
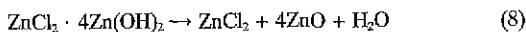


Fig. 7. XRD patterns of dust treated by acid

of Pb at 1100°C completely.⁷⁾

ZnCl₂ (ΔG° : -10.8~-14.6 kcal/mol) was not nearly evaporated at 800°C in oxidation (Eq. 8) due to less vapor pressure than those of PbCl₂ (ΔG° : -24.6~-20.0 kcal/mol) therefore, PbO and PbCl₂ evaporated more easily than ZnCl₂. IR spectra of spinel ferrite (ZnFe₂O₄ and Fe₃O₄)^{7,8)} were denoted by a band, localized at near 585 cm⁻¹ and 465 cm⁻¹. Also, the absorption bands of zinc oxide occurred at 615, 535 and 440 cm⁻¹,¹²⁾ but were not very distinct due to being either just decomposed or very broadened, and hence, were difficult to identify.



3.3. Properties of acid treatment and washing process

Fig. 6 shows that according to the results of IR spectra of dust residues treated by 1N H₂SO₄, the peaks at 3439, 1635, 1026 and 572 cm⁻¹ (Table 3) were clearly observed, and also very weak peaks at 1400 to 1450 cm⁻¹ region, indicated the peaks of Pb(OH)Cl. Considering the results, Pb(OH)Cl was expected to be easily decreased by acid treatment. It was corroborated by XRD analysis of dust that zinc oxide and zinc hydroxyl chloride were almost extracted by 1N H₂SO₄ remaining zinc ferrite as shown in Fig. 7. As a result, IR spectra peaks obtained by acid treatment in Fig. 6 can be considered to be zinc ferrite and iron oxide. In the case of dust residues (float and sink fraction), about 91% of chloride was removed by a washing process.¹⁰⁾ That is, unstable chloride compounds were easily soluble in aqueous solution.

IR spectra of float and sink fraction showed the same peaks at 3449, 1635, 1439, 875, 571 and 455 cm⁻¹. On the contrary, IR absorption bands at the 2942, 2862, 1136 and 1040 cm⁻¹ regions decreased and disappeared by the washing process, which was expected to dissolve the zinc hydroxyl chloride.

4. Conclusion

Electric arc furnace dust generated in Korea consists of 27.5% Fe, 18% Zn, 4.83% Pb and 10.2% CaO and also contains 3.26% Cl and 0.15% F. The strong peaks of zinc ferrite and zinc oxide as major phases and the weaker peaks of lead hydroxyl chloride and sodium chloride were observed using in XRD. The endothermic peak at 134°C corresponds to IR spectra at 2942 and 2862 cm⁻¹ region of dust treated at 200°C. PbCl₂ was decomposed and evaporated at about 500°C and mostly removed at 1100°C. IR spectra of Pb(OH)Cl observed in the 1504 to 1370 cm⁻¹ region with strong distinct doublets, and that of zinc hydroxyl chloride showed the broad absorption peak in the 3600~3200 cm⁻¹ region and the weak band at 1136 and 1040 cm⁻¹ showed a low frequency and these bands splits to 991 and 921 cm⁻¹, thus regarded as ZnO at about 700°C. IR spectra of dust residues treated by 1N H₂SO₄ were observed at 3439, 1635, 1026 and 572 cm⁻¹, and the very weak peak was observed at the 1400 to 1450 cm⁻¹ region, which indicated that the peak of Pb(OH)Cl was easily removed by acid treatment. On the contrary, IR spectra of float and sink fraction by washing process showed the same peaks at 3449, 1635, 1439, 875, 571 and 455 cm⁻¹, but IR absorption bands at the 2942, 2862, 1136 and 1040 cm⁻¹ regions decreased and disappeared using the washing process, which was expected to dissolve the zinc hydroxyl chloride.

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學會誌 投稿 案内

種 類	內 容
論 說	提案, 意見, 批判, 時評
展望, 解説	現況과 將來의 견해, 研究 技術의 綜合解説, Review
技術報告	實際的인 試驗, 調査의 報告
技術, 行政情報	價値있는 技術, 行政情報를 간결히 解説하고, comment를 붙인다.
見 聞 記	國際會議의 報告, 國內外的 研究 幾關의 見學記 등
書 評	
談 話 室	會員相互의 情報交換, 會員 自由스러운 말, 隋霜 등
Group 紹介	企業, 研究幾關, 大學 등의 紹介
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