1   Title

2   Simultaneous degradation and dechlorination of poly (vinyl chloride) by a combination

3   of superheated steam and CaO catalyst/adsorbent

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15   Abstract

16   In order to explore the possibility of efficient chlorine removal from the poly (vinyl

17   chloride) (PVC) containing waste plastics, simultaneous degradation and dechlorination

18   of PVC at a relatively low temperature was investigated by changing the atmosphere gas

19   and metal oxide as catalyst and/or adsorbent (catalyst/adsorbent). 5.0 g of PVC and

20   various metallic oxides such as CaO, Fe_3O_4, SiO_2, Al_2O, $Ca(OH)_2$, MgO were used under

21   the superheated steam and nitrogen atmosphere of 473 K. The degradation rate of the

22   PVC sample was small and the chlorine conversion to inorganic chloride was not

23   observed without catalyst/adsorbent in the presence of either superheated steam or

24   nitrogen atmosphere. Under the superheated steam atmosphere, the CaO

25   catalyst/adsorbent resulted in much larger rates of degradation and dechlorination than

26   any other metal oxides such as Fe_3O_4, SiO_2, Al_2O, $Ca(OH)_2$, MgO compared with

27   nitrogen atmosphere. The calcium compounds such as $CaCl_2$, $CaClOH$ and $Ca(OH)_2$

28   were formed in the sample by the combination of CaO catalyst/adsorbent and superheated

29   steam. The rates of PVC degradation and chlorine conversion to inorganic chlorides were

30   dramatically enhanced beyond the stoichiometric CaO amount for the $CaCl_2$ formation

31   reaction with PVC under the superheated steam atmosphere.

32   The CaO addition contributed to both of the PVC degradation as a catalyst and the

33   reactant with HCl as an adsorbent, whereas the superheated steam played a role of the

34   sample temperature increase to promote the PVC degradation through the exothermic

35   reaction with CaO.

36

37   Key words

38   Dechloriation; waste plastics; PVC; superheated steam; CaO; adsorbent; catalyst；

39   adsorbent

40

1. Introduction

Particular attention is paid to the recent environmental issues on waste plastics washed ashore and accidentally swallowed by marine animals. The proper treatment of waste plastics is important because almost all of them have no biodegradable property and in average contain 10 mass % of polyvinyl chloride (PVC) [1-4]. Ito et al. [5] reviewed various physical and chemical separation techniques of waste plastics by using differences in specific gravity, electrostatic property, wettability, comminuted surface, solubility in organic solvent etc.

On the other hand, it has been pointed out that the thermal degradation, which is viewed as one of the main recycling methods of waste plastics under existing conditions, forms HCl and the other toxic gases due to PVC. They result in the corrosion of metallic equipment and environmental pollution. From this perspective, many researches on the PVC degradation and dechlorination were carried out. The PVC degradation generally occurs in two stages, firstly at a relatively low temperature approximately between 473 and 623 K, and then above approximately 623 K. The lower temperature stage is mainly associated with the HCl formation (dehydrochlorination) and solid residue of polyene structure, whereas the higher temperature stage the polyene breakdown to aromatic hydrocarbons [4, 6-13].

59   The chlorination removal (dechlorination) methods are categorized into two types

60   [3, 14] according to the number of reaction chambers. The first one is to conduct

61   simultaneous dehydrochlorination and dechlorination with catalyst and/or adsorbent

62   (catalyst/adsorbent) at the same spot, and form the dechlorinated products like metallic

63   chlorides [14-27]. The second one is to decompose PVC (dehydrochlorination) at a

64   reaction chamber, and remove chlorine with catalyst/adsorbent from the degradation

65   products such as chlorine-containing gas and oil which are stored at another reaction

66   chamber [14, 28-36].

67   Various catalyst and/or adsorbent (catalyst/adsorbent) [14-36] involving CaO [16,

68   19, 20, 22,27] have been used to accelerate the PVC degradation and dechlorination, and

69   Masuda et al. [21] evaluated the dechlorination behavior of several metal oxides by

70   optical basicity which is widely applied in the fields of glass science and metallurgy to

71   discuss the acidity or basicity of oxides [37]. In addition, there are examples of CaO

72   catalyst/adsorbent use such as a halogen absorber [27, 38-41].

73   Superheated steam has an excellent heat transfer property due to the addition of

74   radiation heat transfer compared with heated air and nitrogen, and the treatment under

75   ordinary pressure permits to reduce the operating cost relatively. It was successfully

76 applied to the dechlorination treatment of municipal solid waste (MSW) [42, 43] and

77 incineration ash [44]. Fonseca et al. [45] investigated the effect of mixed gas of

78 superheated steam and nitrogen without catalyst/adsorbent on the dehydrochlorination of

79 PVC resin and indicated that the dehydrochlorination rate increased from 61 % (100 vol%

80 nitrogen) to 77 % (50 vol% superheated steam – 50 vol % nitrogen) at 523 K by adding

81 superheated steam in nitrogen gas. Superheated steam accelerated the PVC degradation.

82 Hapipi et al. [26] studied the spontaneous dehydrochlorination and dechlorination of PVC

83 with superheated steam and various metal oxides, and obtained the dehydrochlorination

84 rate of 84 % at 473 K with the pure superheated steam atmosphere and the

85 catalyst/adsorbent of 50 mass% ZnO – 50 mass% CoO. Inorganic chloride was also

86 recognized in the sample residue. The PVC dechlorination was enhanced by a

87 combination of superheated steam and catalyst/adsorbent even at a relatively low

88 temperature. However, there were few studies on a combination of CaO

89 catalyst/adsorbent and superheated steam to accelerate the PVC degradation. In addition,

90 the conversion of PVC chlorine into metallic chloride within a reaction chamber is

91 seemed to be more favorable compared to the HCl recovery because the HCl emission

92 out of the chamber causes the metallic corrosion of pipes and devices, and atmospheric

93 pollution, especially in the commercial plant. Thus, further progress in the simultaneous

94 degradation and dechlorination is desired to minimize the HCl emission out of the

95 treatment chamber.

96   In this study, the simultaneous degradation and dechlorination experiments were

97 carried out by using a mixture of PVC and the catalyst/adsorbent except for the metal

98 oxides used in the research by Hapipi et al. [26] as well as both of superheated steam and

99 nitrogen atmospheres at a relatively low temperature. A combination of CaO and

100 superheated steam led to a significant enhancement in the PVC dehydrochlorination as

101 well as the chlorine capture as the inorganic chloride in the sample residue. The formation

102 of inorganic chloride by the degraded HCl reaction with CaO and superheated steam

103 (H_2O) was also discussed. The simultaneous dehydrochlorination and dechlorination with

104 CaO and superheated steam seem to be potentially capable development of an efficient

105 chlorine removal technology from waste plastics because the chlorides remaining in the

106 sample residue were easily removed by water washing.

107

108 2. Experiment

109 2.1 Sample preparation

110   5.0 g of PVC resin powder (FUJIFILM Wako Pure Chemical Corp.) was used as a

111   feedstock. The catalyst/adsorbents in this experiment were CaO, Al_2O_3, SiO_2, Fe_3O_4, MgO

112   and $Ca(OH)_2$ and those mass was kept to 5.0 or 5.8 g, although the CaO in mass was

113   varied to 1.0, 2.0, 3.0, 4.0, 5.0 and 5.8 g. The PVC and catalyst/adsorbent were mixed

114   physically by a mortar and compressed to a pellet under 60 MPa using a hydraulic press

115   to make it easy to put on the sample basket of the experimental device. The pellet size for

116   5.0 g of PVC and 5.8 g of catalyst/adsorbent is 1.0 x 8.5 x 0.5 cm.

117

118   2.2 Experimental apparatus and procedure

119   A schematic diagram of superheated steam apparatus (Hi-Heater 2005S, Dai-ichi

120   High Frequency Co., Ltd.) is shown in Fig. 1. It was composed of a boiler, superheated

121   steam generator and reaction chamber. The superheated steam was adjusted to a setting

122   temperature of 473 K and provided to the reaction chamber. A sample was charged in the

123   reaction chamber filled with the superheated steam of 473 K and the experiment was

124   commenced. The temperatures of the sample and superheated steam were measured by

125   thermocouples A and B, respectively, as shown in Fig. 1. However, since the temperature

126   of the sample with CaO catalyst/adsorbent increased rapidly just after charging into the

8

127   reaction chamber filled with superheated steam, it was brought close to 473 K within

128   about 5 min by reducing the input superheated steam temperature to around 453 K. The

129   treatment time and flow rate of superheated steam were fixed to 60 min and 10 kg/h,

130   respectively, as described by Hapipi et al. [26]. After the experiment, the sample was

131   cooled to the room temperature before drawn out of the chamber and dried at 383 K in a

132   drier for 24 hour before the measurement of its mass.

133   The nitrogen pyrolysis was conducted by using an electric furnace (TMF-500N, As

134   One Co., Ltd.) as schematically shown in Fig. 2. The treatment time and setting

135   temperature measured by thermocouples A and B in Fig. 2 were 60 min and 473 K,

136   respectively, which were similar to the superheated steam conditions. Nitrogen flow rate

137   was fixed at 6.0 kg/h. The difference of gas flow rate between superheated steam and

138   nitrogen seems to affect a negligible change in the PVC degradation and dechlorination

139   at 60 min of treatment time because Hapipi et al. [26] showed that the PVC degradation

140   was almost terminated after 30 min of treatment time by the same devices.

141

142   2.3 Chlorine and XRD analyses

143   The procedure of chlorine analysis is as follows. 1.5 g of dried sample after the

144   experiment was treated with 100 mL of hot water for 30 min, and then filtered to obtain

145   inorganic chlorine solution. Chlorine in the solution was analyzed by the mercury

146   thiocyanate absorption photometry method [46]. The organic chlorine content in the

147   sample was analyzed by the residue on the filter paper formerly used for the separation

148   of the inorganic chloride. 1.0 g of residue sample after dried at 383 K in a drier for 24

149   hour and 3.0 g of Eschka blending agent [26, 47] were mixed and calcined at 948 K for

150   90 min and filtered to achieve inorganic chlorine solution. The residue-induced chlorine

151   (organic chlorine) was also detected by the mercury thiocyanate absorption photometry

152   method [47].

153   Gas analysis was not carried out in this study because the PVC degradation

154   resulted in the production of HCl and a solid residue at the relatively lower temperature

155   of 473 K as indicated by Yoshioka et al. [13]. However, the gas components should be

156   analyzed at the higher temperature where various gas and liquid generate in addition to

157   HCl.

158   The X-ray diffraction patterns were analyzed by an XRD (RINT 2100, Rigaku

159   Corp.) for the treated samples of a mixture of 5.0 g of PVC and 5.0 g of CaO under

160   superheated steam and nitrogen atmospheres after cooled to the room temperature.

161

162   2.4 Evaluation of dechlorination behavior

163   The dechlorination rate, R [%], from the PVC sample was defined as Eq. (1).

164    $$R = \frac{(Cl_0 - Cl_{\text{organic}})}{Cl_0} \times 100 \qquad\qquad (1)$$

165   where Cl_0 is the mass of chlorine in the PVC sample (=5.0x56.8/100=2.84 g) before the

166   treatment and Cl_{organic} is the mass [g] of organic chlorine after the treatment obtained

167   from the organic chlorine analysis of the sample residue.

168   The conversion rate, C [%], from organic to inorganic chlorine in the treated

169   sample is defined as Eq. (2).

170    $$C = \frac{Cl_{\text{inorganic}}}{Cl_0} \times 100 \qquad\qquad (2)$$

171   Here, $Cl_{\text{inorganic}}$ is the mass [g] of inorganic chlorine after the treatment obtained from

172   the inorganic chlorine analysis.

173   The volatile chlorine was given by subtracting the inorganic and organic chlorines

174   in the treated sample from the PVC chlorine.

175

176   3. Results and discussion

177   3.1 Effect of atmosphere gas on dechlorination behavior without catalyst/adsorbent

178   The effect of atmosphere gas on the percentage of volatile and organic chlorine

179   amounts after the treatment are shown in Fig. 3. The catalyst/adsorbent was not used

180   here. Chlorine was classified in terms of organic (unreacted) and volatile chlorine.

181   There was no inorganic chlorine in the sample. The values of dechlorination rate, R [%],

182   under superheated and nitrogen atmospheres were small and remained at the level of 14

183   and 20 %, respectively.

184

185   3.2 Effect of metal oxide on dechlorination behavior under superheated steam

186   atmosphere

187   The effect of 5.8 g of metal oxide on the percentage of volatile, inorganic and organic

188   chlorine amounts after the treatment are shown in Fig. 4. The dechlorination behavior

189   was compared between no-catalyst/adsorbent, Al_2O_3, CaO, SiO_2 and Fe_3O_4 under the

190   superheated steam atmosphere. There were two kinds of chlorine in the sample residue

191   after the treatment; organic and inorganic chlorides. From the organic chlorine content,

192   the values of dechlorination rate, R, was in the order of CaO $\gg$ Fe_3O_4 >SiO_2 > Al_2O_3>

193   No-catalyst/adsorbent. The R and C values of CaO achieved 93 and 80 %, respectively.

194   The added CaO played two roles; a catalyst for the PVC degradation and an adsorbent for

195   the decomposed HCl to form inorganic chlorides. In the case of CaO catalyst/adsorbent,

196   the maximum sample temperature augmentation reached 50 deg just after charging the

197   sample into the reaction chamber for the experiment, although it was reduced to 473 K

198   within 5 min. The initial temperature increase is estimated to affect the promotion of the

199   R and C values. This will be discussed in Section 3.4. R= 93 % of CaO

200   catalyst/adsorbent in this study was larger than R = 84 % of 5.8 g of 50 mass % ZnO-50

201   mass% CoO catalyst/adsorbent obtained by Hapipi et al. [26] as mentioned in the

202   introduction. There was no inorganic chlorine content in the sample residue of Fe_3O_4,

203   SiO_2 and Al_2O_3 catalyst/adsorbents in Fig. 4. That indicates that these metallic oxides

204   have catalytic ability only but no adsorption one.

205

206 ### 3.3 Effect of alkaline earth metal compounds on dechlorination behavior under

207 superheated steam atmosphere

208   The effect of 5.0 g of alkaline earth metal compounds such as CaO, $Ca(OH)_2$ and

209 MgO on the percentage of volatile, inorganic and organic chlorine amounts after the

210 treatment is shown in Fig. 5. The atmosphere was superheated steam. Chlorine was

211 captured in the sample residue as inorganic chloride when CaO, $Ca(OH)_2$ and MgO

212 catalyst/adsorbents were used. 5.0 g of CaO addition promoted the PVC degradation

213 and chlorine capture in the sample residue like 5.8 g of CaO catalyst/adsorbent in Fig. 4,

214 and the R and C values reached 95 and 91 %, respectively. On the other hand, the R and

215 C values of $Ca(OH)_2$ addition became 55 % and 5.4 %, respectively, which means that

216 $Ca(OH)_2$ had only a good catalytic ability, although it was lower level than CaO. The

217 reason will be discussed in Section 3.4. The MgO addition resulted in $R = 38$ % and C

218 $= 9.3$ %, which indicated the lower catalyst/adsorbent ability than CaO and $Ca(OH)_2$.

219

220 ### 3.4 Comparison of dechlorination behavior with CaO catalyst/adsorbent between
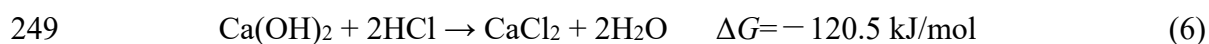
221 superheated and nitrogen atmospheres

222   From the above results, both the dehydrochlorination and dechlorination rates

223   increased drastically under superheated steam atmosphere when CaO catalyst/adsorbent

224   was added. In this section, the effect of dechlorination behavior with 5.0 g of CaO

225   addition was compared between superheated steam and nitrogen atmospheres as shown

226   in Fig. 6. The R and C values of the superheated steam atmosphere became 95 and

227   91 %, respectively, whereas the dechlorination under nitrogen atmosphere dropped

228   down to R=44 % and C=4.4 %. Superheated steam played an important role to promote

229   the PVC dechlorination at CaO addition.

230   To identify the inorganic chloride in the sample residue, the XRD patterns under

231   superheated steam and nitrogen atmospheres were analyzed as shown in Figs. 7 and 8,

232   respectively. Under the superheated steam atmosphere in Fig. 7, there were presence of

233    $Ca(OH)_2$, CaClOH and $CaCl_2$ · $6H_2O$ as well as CaO. $CaCl_2 \cdot 6H_2O$ is formed only

234   below 303 K as indicted in the phase diagram of calcium chloride and water [48], and

235   calcium-containing chloride at the atmospheric temperature of 473 K exists as $CaCl_2$ or

236    $CaCl_2 \cdot 1/3H_2O$ [49, 50]. $CaCl_2 \cdot 6H_2O$ is considered to be generated by the hydration

237   process when the sample is cooled to the room temperature after the experiment.

238   CaClOH and $Ca(OH)_2$ are found at both 473 K and the room temperature [51]. On the

15

239   other hand, under the nitrogen atmosphere in Fig. 8, there was no inorganic chloride,

240   but CaO and $Ca(OH)_2$. $Ca(OH)_2$ seems to come into existence because of the reaction of

241   CaO with H_2O in the air during the measurement setup and sample preservation.

242   Next, the inorganic chloride formation is discussed based on the above

243   explanation. CaO reacts with HCl and/or H_2O to evolve calcium compounds such as

244     $CaCl_2$[52], CaClOH [51-53] and $Ca(OH)_2$ [52], and the reaction of $Ca(OH)_2$ with HCl

245   leads to $CaCl_2$ [52] by the following reaction formulae:

246          $CaO + 2HCl \rightarrow CaCl_2 + H_2O$ $\Delta G = -162.1$ kJ/mol   (3)

247          $CaO + HCl \rightarrow CaClOH$ $\Delta G = -27.9$ kJ/mol   (4)

248          $CaO + H_2O \rightarrow Ca(OH)_2$ $\Delta G = -41.7$ kJ/mol   (5)

249          $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$ $\Delta G = -120.5$ kJ/mol   (6)

250   Here, the values of the change in Gibbs free energy, ΔG [kJ/mol], at 473 K were also

251   shown in Eqs. (3) - (6). The negative ΔG values of Eqs. (3) and (6) indicated that these

252   reactions proceed theoretically. It was also found that H_2O was not involved in the

253   formation of calcium-containing chlorides such as $CaCl_2$ and CaClOH.

16

254   The dechlorination procedure with a combination of CaO and superheated steam

255   (H_2O) is estimated as follows: The temperature enhancement is first caused by the

256   exothermic reaction of CaO with H_2O as shown in Eq. (5), which promotes the PVC

257   degradation [26,27]. The formed HCl reacts with CaO and $Ca(OH)_2$, and easily

258   produces the calcium chlorides such as $CaCl_2$ and CaClOH. The smaller amount of

259   dechlorination with combinations of CaO and N_2 in Fig. 6, and $Ca(OH)_2$ and H_2O in

260   Fig. 5 is due to the less temperature increase to encourage the PVC degradation under

261   the relatively low pyrolysis temperature.

262   As indicated in Section 3.2, the initial rapid temperature increase in the CaO-

263   containing sample under the superheated steam atmosphere was up to 50 deg. It is

264   explained as follows: The heat, ΔH, of exothermic reaction with CaO and H_2O is

265   1.9×10^3 J/g at 473 K [52], and the sample heat capacity, C_p, per gram in average is

266   assumed to be 1.0 J/g•K due to C_p of PVC of 1.2, CaO of 0.8, and $Ca(OH)_2$ of 1.2

267   J/g•K. When 5 mass % of 5.8 g of CaO (mass of CaO reacting with H_2O, m_{CaO} : 5.8 x

268   0.05 = 0.29 g) reacts with H_2O just after charging into the reaction chamber, the

269   temperature increase, ΔT, caused by the $Ca(OH)_2$ formation is calculated as 51 deg

270   according to the simple heat balance equation of $w\, C_p\, \Delta T = m_{CaO}\, \Delta H$. Here, w [g] is the

17

271   mass of total sample (=5.0 (PVC) + 5.8 (CaO) = 10.8 g). Thus, the initial temperature

272   increase under the combination of CaO and superheated steam was explained by the

273   exothermic reaction of about 5 mass % of CaO and H_2O. The exothermic $Ca(OH)_2$

274   formation reaction also proceeds in the sample temperature-descending process caused

275   by the decrease in the input superheated steam temperature. This temperature

276   enhancement is estimated to promote the PVC degradation and dechlorination.

277

278   3.5 Effect of CaO amount on dechlorination behavior under superheated steam

279   atmosphere

280   When CaO in PVC converts to $CaCl_2$, the stoichiometric CaO amount, w_s [g], for

281   5.0 g of PVC is calculated as follows:

282       $w_s = 5.0 \times M_{CaO}/(2M_{C2H3Cl})=5.0 \times 56/(2 \times 62.5)=2.24$ g   (8)

283   Here, M_{CaO} and M_{C2H3Cl} are the molecular mass of CaO and C_2H_3Cl, respectively. Fig. 9

284   shows the effect of CaO amount, w_{CaO}/w_s, normalized by the stoichiometric mass of

285   CaO on the percentage of volatile, inorganic and organic chlorine amounts after the

286   treatment under the superheated steam atmosphere. Here, w_{CaO} [g] is the initial mass of

287   CaO in PVC. The values of R and C changed significantly from 68 % to 88 %, and from

288   14 % to 26 %, respectively, between normalized CaO amount of 0.89 and 1.34. The R

289   and C values increased with the increasing w_{CaO} beyond w_{CaO}/w_s of 1 and reached 95

290   and 91 %, respectively, at w_{CaO}/w_s= 2.23 (w_{CaO} =5.0 g). The CaO amount required for

291   almost all PVC dehydrochlorination and chlorine capture in the sample was about twice

292   as large as the stoichiometric CaO amount.

293

294   3.6 PVC dechlorination by a combination of CaO and superheated steam

295   Rearranging the data of Figs. 3-6 and 9, the relationship between C and R is shown

296   in Fig. 10. There are three possibilities for the PVC degradation and dechlorination: i) all

297   dehydrochlorinated chlorine is absorbed as inorganic chloride indicated by line p, ii) part

298   of chlorine still remains as the polymer, and iii) all dehydrochlorinated chlorine is

299   released as HCl or volatile organic chlorinated compounds which results in a line equal

300   to the X-axis. Although the conversion of dehydrochlorinated chlorine into inorganic

301   chloride was not much proceed at $R \leq 70$ % under various catalyst/adsorbents used in this

302   study, the CaO catalyst/adsorbent with superheated steam indicated the exponential

303   acceleration of the C value at $R > 70$ %. As indicated in Section 3.5, the higher C value of

304   the CaO catalyst/adsorbent at $R>70$ % responded to the excessive CaO amount to

305   stoichiometric one.

306   As described above, the PVC degradation and chlorine conversion to the inorganic

307   calcium chloride in the sample residue were dramatically enhanced by a combination of

308   CaO addition and superheated steam atmosphere. This mechanism is schematically

309   summarized in Fig. 11. The part of CaO with superheated steam (H_2O) is initially reacted

310   exothermically and $Ca(OH)_2$ is formed, which causes the rapid enhancement in the

311   sample temperature. The temperature increase accelerates the PVC degradation and

312   dechlorination. CaO and $Ca(OH)_2$ behave as a catalyst to promote the

313   dehydrochlorination by involving the selective cleavage of C - Cl bonds [1] and then

314   contribute to the chlorine adsorption in the sample residue by calcium chloride formation.

315   The PVC dehydrochlorination generates the evolution of gaseous species such as HCl

316   and gives some void space in the sample pellet. The surrounding CaO and $Ca(OH)_2$ as

317   adsorbents are reacted with the volatile HCl.

318   Simultaneous degradation and dechlorination processes for recycling chlorine-

319   containing waste plastics may be expected to be developed by a combination of CaO and

320   superheated steam in the next stage.

321

322 4. Conclusions

323   Effects of atmosphere gas and catalyst/adsorbent on the simultaneous

324 dehydrochlorination and dechlorination of PVC were investigated in this study.

325 (1) The degradation rate of the PVC sample was small and the chlorine conversion to

326   inorganic chloride was not recognized without catalyst/adsorbent in the presence of

327   either superheated steam or nitrogen atmosphere.

328 (2) Under the superheated steam atmosphere, the CaO catalyst/adsorbent indicated much

329   larger rates of dechlorination from the PVC sample and volatile chlorine capture as

330   inorganic chlorides than any other metal oxides such as Fe_3O_4, SiO_2, Al_2O, $Ca(OH)_2$,

331   MgO. The dechlorination rate from the PVC sample with the metal oxides in this

332   study was higher than that without metal oxides.

333 (3) The CaO catalyst/adsorbent under the superheated steam atmosphere resulted in

334   larger rates of dechlorination from the PVC sample and chlorine conversion to

335   inorganic chlorides than that under nitrogen. During the CaO catalyst/adsorbent

336 treatment under the superheated steam atmosphere, $CaCl_2$ (or $CaCl_2 \cdot 1/3H_2O$),

337 CaClOH and $Ca(OH)_2$ were estimated to be formed in the sample.

338 (4) Under the superheated steam atmosphere, the rates of dechlorination from the PVC

339 sample and conversion to inorganic chlorides were dramatically enhanced above the

340 stoichiometric CaO amount for the $CaCl_2$ formation reaction with PVC and H_2O.

341 (5) The dechlorination with a combination of CaO and superheated steam was estimated

342 to proceed as follows: The temperature enhancement is first caused by the exothermic

343 reaction of CaO with H_2O and promotes the PVC degradation. Next, the formed HCl

344 reacts with CaO and $Ca(OH)_2$, and becomes the calcium chlorides such as $CaCl_2$ and

345 CaClOH. The CaO addition contributed to both of the PVC degradation and the

346 reaction with HCl, and superheated steam also played two roles of the temperature

347 increase promoting the PVC degradation and a reactant with HCl.

348

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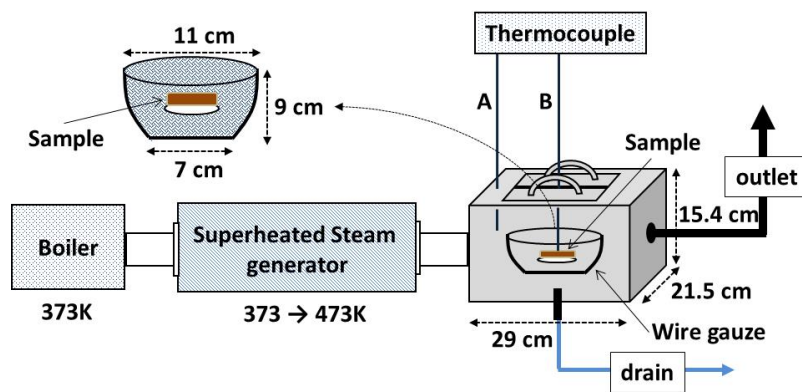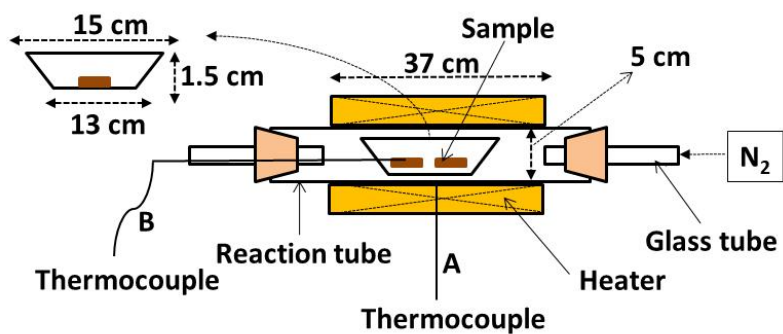

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481   Caption list

482   Fig. 1 Schematic diagram of superheated steam device used for the experiment.

483   Fig. 2 Schematic diagram of electric furnace under nitrogen atmosphere used for the

484   experiment.

485   Fig. 3 Effect of atmosphere gas on percentage of volatile and organic chlorine amounts

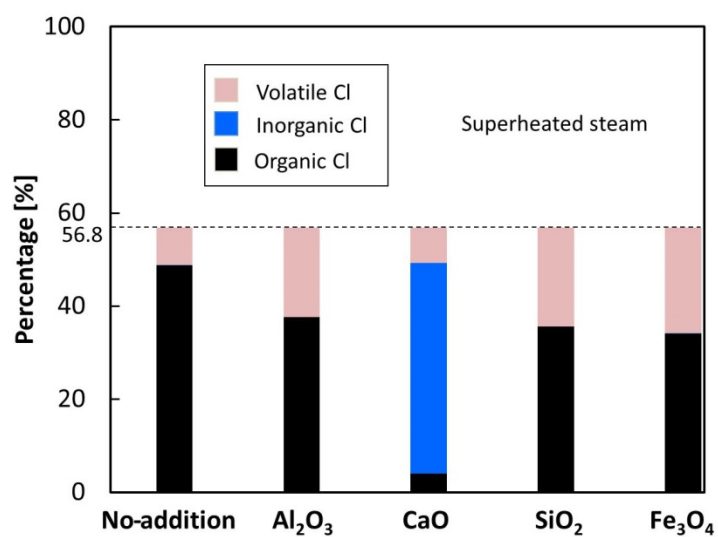486   without catalyst/adsorbent.

487   Fig. 4 Effect of metal oxide on percentage of volatile, inorganic and organic chlorine

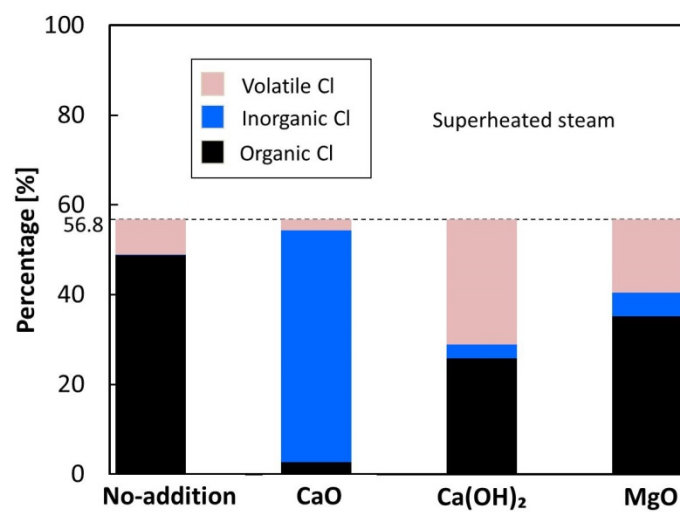488   amounts under superheated steam atmosphere.

489   Fig. 5 Effect of alkaline earth metal compound on percentage of volatile, inorganic and

490   organic chlorine amounts under superheated steam atmosphere.
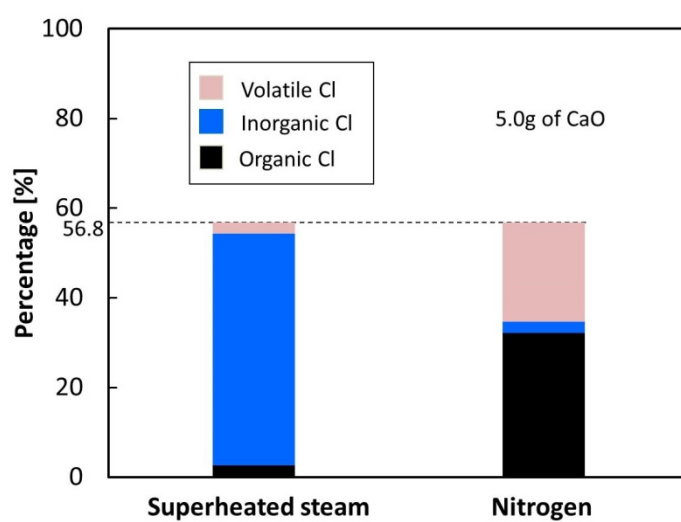
491   Fig. 6 Effect of atmosphere gas on percentage of volatile, inorganic and organic

492   chlorine amount with CaO catalyst/adsorbent.

493   Fig. 7 X-ray diffraction patterns with a combination of CaO and superheated steam.

494   Fig. 8 X-ray diffraction patterns with a combination of CaO and nitrogen.

495   Fig. 9 Effect of CaO amount on percentage of volatile, inorganic and organic chlorine

496   under superheated steam atmosphere.

497   Fig. 10 Relationship between chlorine conversion ratio to inorganic chloride and

498   dechlorination rate.

499   Fig. 11 Functions of CaO and superheated steam for PVC degradation and HCl

500   conversion to calcium-based chloride.

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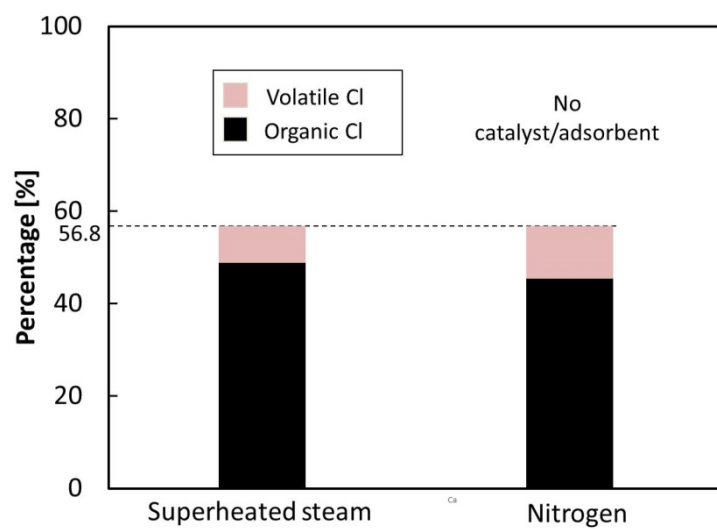
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519   Fig. 3 Effect of atmosphere gas on percentage of volatile and organic chlorine amounts

520   without catalyst/adsorbent.

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Fig. 4 Effect of metal oxide on percentage of volatile, inorganic and organic chlorine

amounts under superheated steam atmosphere.

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Fig. 5 Effect of alkaline earth metal compound on and percentage of volatile, inorganic

and organic chlorine amounts under superheated steam atmosphere.

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Fig. 6 Effect of atmosphere gas on and percentage of volatile, inorganic and organic

chlorine amount with CaO catalyst/adsorbent.
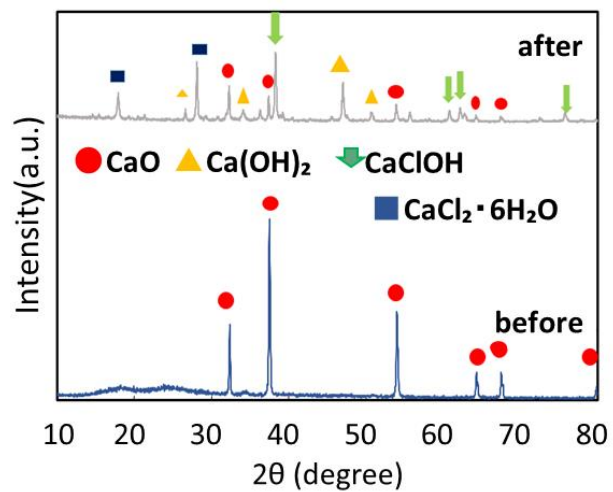
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547 Fig. 7 X-ray diffraction patterns with a combination of CaO and superheated steam.

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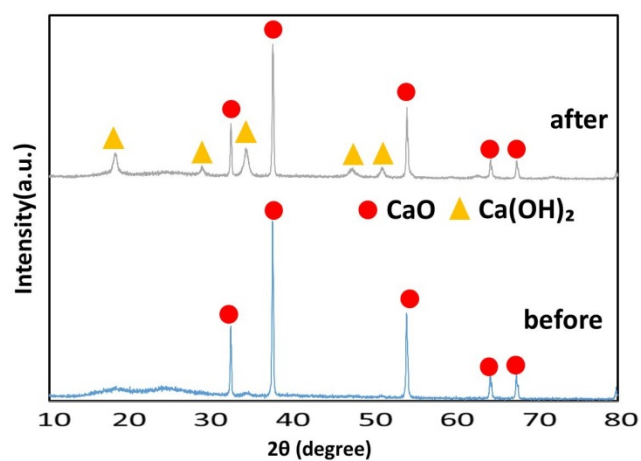
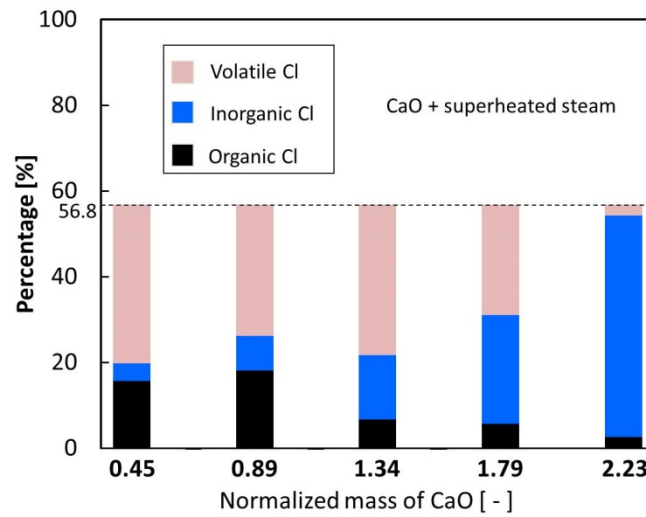Fig. 8 X-ray diffraction patterns with a combination of CaO and nitrogen.

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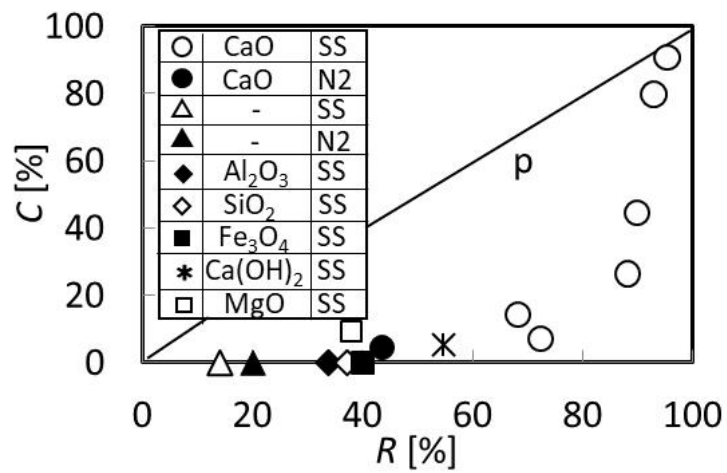

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559   Fig. 9 Effect of CaO amount on and percentage of volatile, inorganic and organic

560   chlorine under superheated steam atmosphere.

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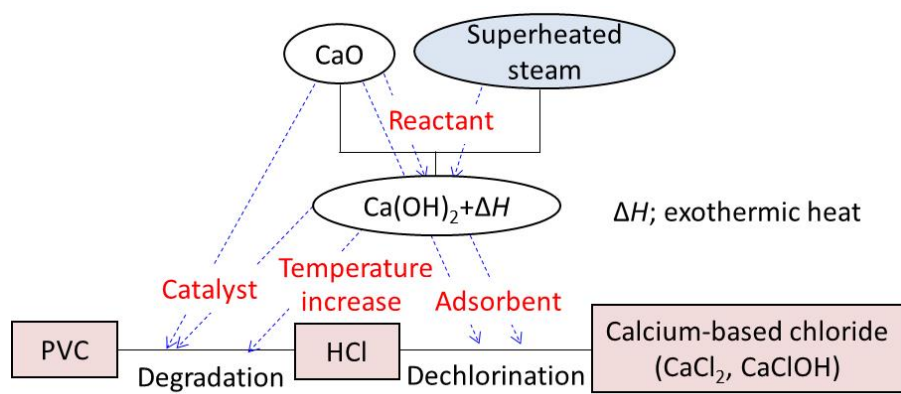
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