

## Effects of $\text{CaCO}_3$ filler on dechlorination rate of PVC wire and cable sheath materials

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Effect of  $\text{CaCO}_3$  filler amount on deHCl gas is evaluated in paper. In test,  $\text{CaCO}_3$  filler is varied as 0, 35 or 70 phr and heat decomposition temperature is varied as  $250^\circ\text{C} \sim 400^\circ\text{C}$ . After test, Relationship between deHCl gas and  $\text{CaCO}_3$  filler in PVC compound is evaluated and Activation energy is calculated as  $62.2\text{kJ/mol}$  ( $14.8\text{ kcal/mol}$ ). It becomes clear that as  $\text{CaCO}_3$  filler in PVC compound increases, inorganic chloride in heat decomposition residues increases.

### 1. Introduction

For the composition of compounds for PVC wire and cable sheath materials, the polymerization degree of the PVC resin used is wide and several plasticizers, lubricants, stabilizers, fillers and flame retardant materials are combined to make optimal processing ability applicable to the wire and cable shape and/or thickness of the sheath.

The calcium carbonate is generally used for the filler, one of compounding agents for PVC wire and cable, in order to improve the functionality and increase its volume.

It is also known that the calcium carbonate is a compound, which captures hydrogen chloride produced when the PVC burns. However, there is much to be found about the chloride capturing effects.

In this experiment, effects of the calcium carbonate on dechlorination reaction of PVC at relatively low temperatures ( $250 - 400^\circ\text{C}$ ) were studied. This paper reports the results of the experiment.

### 2. Experiment method

#### 1) PVC compounding and conditioning method

Three kinds of compound compositions shown in Table 1 were conditioned. As can be seen in the Table,  $\text{CaCO}_3$ , a filler of compounds for PVC wire and cable sheath materials, was determined as a variable and three levels, 0, 35 or 75 phr.

When making compound samples, the compound was melted entirely at  $160 - 175^\circ\text{C}$  using

the roll mill, mixed for 10 – 15 min., and press-formed at 180°C for 5 – 10 min. to make a sheet with a thickness of 1 mm.

Table 1 Compounding composition [Unit: PHR]

Compounding agent	M-1	M-2	M-3	Remarks
PVC	100	100	100	SG1300(MitsubishiChemicalMKV)
DOP	50	50	50	DOP(Mitsubishi Chemical)
Calcium carbonate	75	35	0	Softon (Bihoku Powder Chemical)
Tribasic sulfate lead	4	4	4	TL-4000(Sakai Kagaku)
Stearic acid Ba	1	1	1	SB(Sakai Kagaku)
Total	230	190	155	

## 2) Accelerated deterioration conditions

To check the relationship between the secular deterioration and dechlorination rate of the PVC wire and cable sheath material, each sample was tested for accelerated deterioration caused by heat. The accelerated deterioration conditions were calculated assuming that the operating temperature of the PVC wire and cable is 60°C and the heat deterioration activation energy is 181KJ/mol(43 Kcal/mol). That is, 100°C x 86 hrs. or 100°C x 172 hrs. was substituted for 10-year deterioration or 20-year deterioration, respectively (See Table 2). The gear-oven was used for heating.

Table 2 Accelerated deterioration conditions

Original	No accelerated deterioration
Equivalent to 10-year aging	100°C x 86 hrs.
Equivalent to 20-year aging	100°C x 172 hrs.

## 3) Heat decomposition test and hydrogen chloride production rate measurement

The heat decomposition test was made on the accelerated deterioration samples shown in Table 2 under temperature conditions stated in Table 3 to check the hydrogen chloride production rate per hour. The test was made with n = 1 – 2 at each temperature. Nitrogen gas was used for the heat decomposition atmosphere.

Described below is the procedures used to measure of the hydrogen chloride production rate.

(1) Conditioning of samples: PVC sheet conditioned in step 2) was cut to 2 – 3 mm-square sample pieces so that each sample piece weighs approximately 0.7 g.

(2) Experimental apparatus:

The experimental apparatus conforming to JCS No. 397 (1992) (See Fig. 1). Table 4 shows the difference when compared to IEC60754 (1994).

The air pump gas passing through the enriched acetic acid and silica gel was used as introduction gas. The gas flow rate of 160 ml/min. was used based on the calculation formula defined in IEC.

Table 3 Heat decomposition conditions

Temperature (°C)	Time (Min.)			
250	10	20	40	80
300	10	15	20	30
350	5	10	15	20
400	5	10	15	—

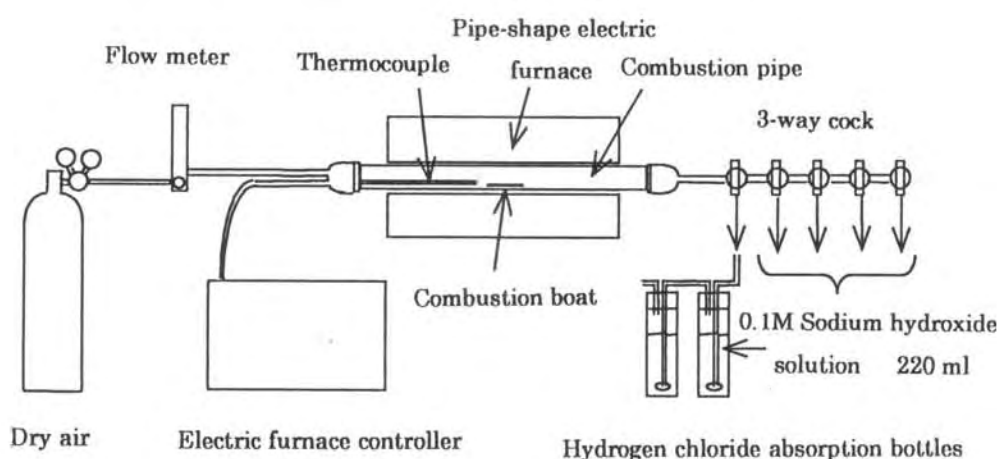


Fig. 1 Hydrogen chloride capturing unit

Table 4 Specifications for heat decomposition unit used

	IEC	This experiment
Size of combustion furnace (mm x mm)	500~600 × 40~60	300 × 98
Inner diameter of combustion pipe (mm)	32~45	25
Length of combustion port (mm)	45~100	67
Width (mm)	12~30	12
Depth (mm)	5~10	10
Gas absorption bottles connected	Twin bottles	4 sets of twin bottles in parallel

## (3) Hydrogen chloride production rate:

The titration and production volume calculation of the hydrogen chloride were made in conformity with the IEC standards. The calculation formula is shown below.

Hydrogen chloride production volume (mg/g) =  $(36.5 (B - A) M \times 1000/20) / m$

Where,

A: 0.1M thiocyanic acid ammonium solution volume necessary for titration of silver nitrate solution (ml)

B: 0.1M thiocyanic acid ammonium solution volume necessary for titration in the idling-test (test with no sample in combustion pipe) (ml)

M: Molar value of thiocyanic acid ammonium solution

m: PVC compound weight (g)

In addition, the measurement of the heat decomposition residue and the chlorine analysis of the heat decomposition residue were made.

## (4) Heat decomposition residue volume:

The weight of the sample before and after the heat decomposition was measured accurately.

The heat decomposition residue volume was calculated from the following formula.

Residue volume (wt%) =  $\text{Weight (g) after heat decomposition} / \text{Weight (g) before heat decomposition} \times 100$

## (5) Chlorine analysis of heat decomposition residue:

The heat decomposition residue was pulverized and dried under reduced pressure and using that as samples, the following items were measured.

① Total chlorine: The sample was combusted completely in the oxygen flask combustion unit. The combustion exhaust gas was absorbed through the alkaline solution and the chloride ion contained in the absorbed solution was measured using the ion chromatography.

② Inorganic chlorine: After the sample was agitated and extracted in the de-ionized water, the chloride ion in the water tank was measured using the ion chromatography.

③ Organic chlorine: After the inorganic chlorine was extracted, the insoluble contents were filtered, washed, and dried. The organic chlorine was measured using the dried sample by means of the method in conformity with the total chlorine analysis method.

### 3. Results and investigations

Figs. 2 (a) - (d) show the summary of the secular changes of the dechlorination rate. Since the logical hydrogen chloride content in each compound sample varies (see Table 5), the

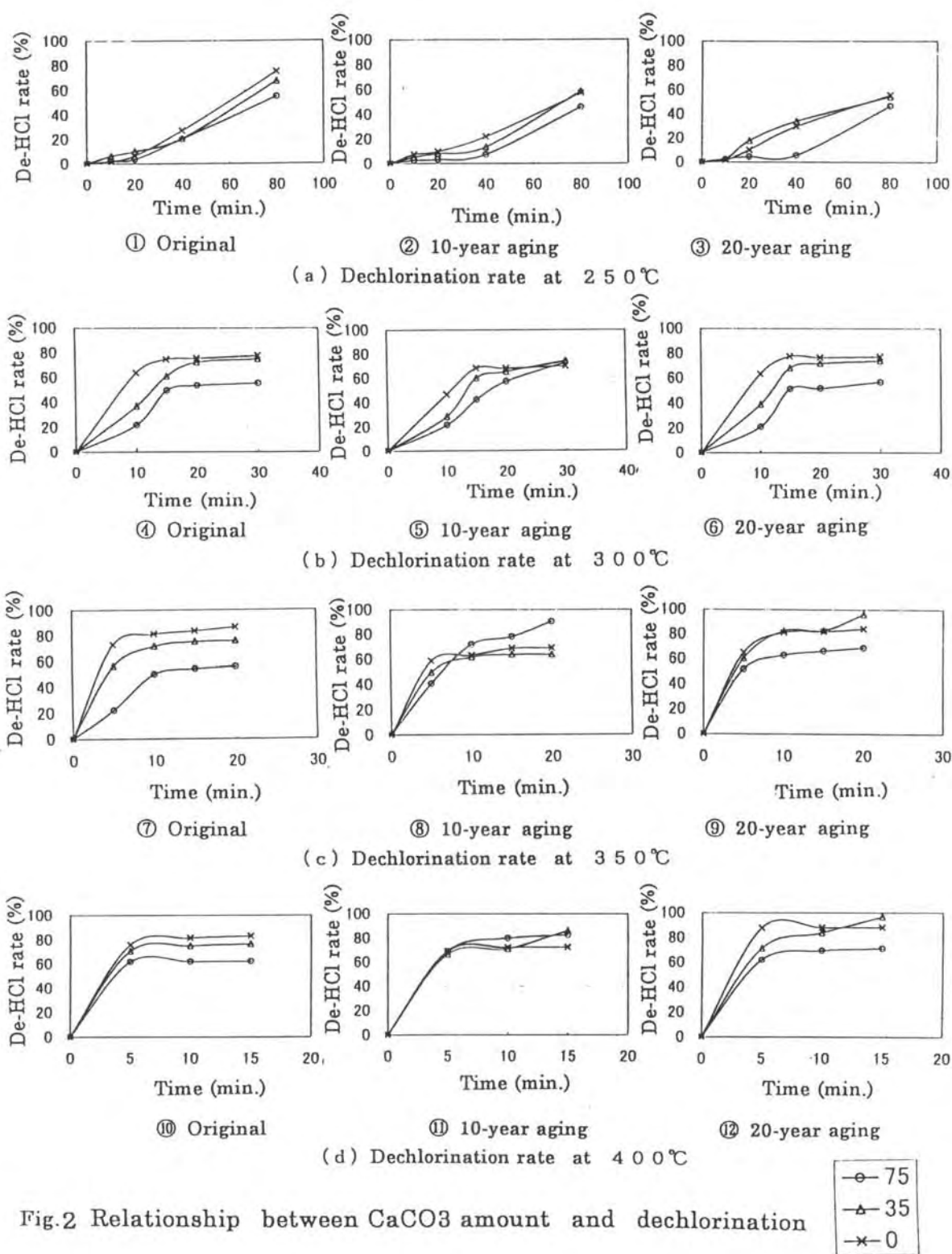


Fig.2 Relationship between  $\text{CaCO}_3$  amount and dechlorination

hydrogen chloride production rate is defined as "dechlorination rate", which is obtained when the hydrogen chloride content in each original sample is determined as 100.

Table 5 Theoretical content of hydrogen chloride content

	M-1	M-2	M-3
Theoretical content (wt%) of hydrogen chloride content	25.4	30.7	37.7

The findings obtained from these results are as follows:

### 1) Heat decomposition curve

The dechlorination reaction of both the original and aged samples is almost completed within the measurement time (about 20 min. after starting of the test) when the heat decomposition temperature is 300 °C and higher. On the other hand, when the heat decomposition temperature is 250 °C, it is determined that the dechlorination reaction is completed after 80 min. since the measurement is completed in the rising portion of the heat decomposition curve. In either case, as the amount of calcium carbonate compound becomes larger, the apparent dechlorination rate lowers. This is because the calcium carbonate reacts with the hydrogen chloride produced by the heat decomposition and becomes the calcium chloride. This calcium chloride traps a part of the hydrogen chloride produced.

### 2) Dechlorination reaction

#### ① Heat decomposition curve of original sample

The dechlorination rate is the largest in M-3, and then M-2, and M-1, in that order at any heat decomposition temperature. It is thought that the calcium carbonate traps a part of the hydrogen chloride produced by the heat decomposition.

#### ② Heat decomposition curve of samples equivalent to 10-year or 20-year aging

It was not clearly confirmed that the dechlorination rate of the sample equivalent to 10-year or 20-year aging is affected by the calcium carbonate compound amount. Presumably this is because in the sample before heat decomposition the hydrogen chloride produced during heating of the promoted deterioration reacts with the calcium carbonate of the filler and thus the hydrogen chloride capturing capability of the calcium carbonate is changed.

### 3) Heat decomposition residue amount

The trend of the heat decomposition residue against the calcium carbonate compound amount is the same as that of the original sample and samples equivalent to 10-year and 20-year

aging.

The larger the calcium carbonate compound amount is, the larger the heat decomposition residue becomes (see Table 6.) This is because the inorganic filler compound amount affects the residue. In addition, the residue tends to increase slightly as the deterioration of the sample is promoted. The weight decrease of the original sheet is confirmed during promoted-deterioration as shown in Table 7 and supposedly it is caused by scattering of plasticizer and promotion of dechlorination.

Therefore, when the sample equivalent to aging is compared to the original sample, the organic content (mainly plasticizer) is volatilized as the deterioration is promoted, and as a result, the heat decomposition residue is increased slightly.

Table 6 Relationship among temperature, amount of calcium carbonate, and heat decomposition residue

Temperature (°C)	Calcium carbonate (wt%)	Heat decomposition residue (wt%)		
		Initial	10-year aging	20-year aging
250	0	41.4	51.2	44.8
	35	60.2	60.2	64.1
	75	62.2	62.2	72.8
300	0	29.0	30.2	30.5
	35	44.9	45.4	46.1
	75	55.3	55.9	56.8
350	0	26.2	27.0	27.5
	35	42.4	42.7	44.0
	75	53.2	54.2	55.9
400	0	21.0	21.9	22.4
	35	38.3	40.3	39.7
	75	50.6	52.2	52.1

Table 7 Weight decrease by promoted-deterioration [Unit: wt%]

	M-1	M-2	M-3
10-year aging	1.8	2.1	2.4
20-year aging	3.5	4.1	4.6

#### 4) Chlorine analysis of heat decomposition residue

The analysis results of the residue after the heat decomposition of the original sample at 350°C are shown in Table 8. Most of the chloride residue of the calcium carbonate compound (M-1, M-2) is inorganic chloride. This is supposedly because the hydrogen chloride produced by heat decomposition reacts with the calcium carbonate to produce the calcium chloride. Assuming that all of the inorganic chloride is calcium chloride, calculation shows that 21.4% (M-2) - 22.4% (M-1) of the compound calcium carbonate reacts with the chloride.

Also, using the analysis results, the material balance of the chlorine compound in the PVC was calculated and the results are shown in Table 9. In the case of M-3 which does not include the filler compound, the dechlorination rate, organic chlorine, inorganic chlorine and unknown/error, are 86%, 1.4%, 0.4%, and 12%, respectively.

Table 8 Results of decomposition residue analysis (wt%)

Composition	Total chlorine	Inorganic chlorine	Organic chlorine
M-1	10.4	9.3	0.7
M-2	7.9	6.3	1.3
M-3	2.5	0.6	2.0

Table 9 Material balance of chlorine

Composition	M-1		M-2		M-3	
	Wt%	Ratio (%)	Wt%	Ratio (%)	Wt%	Ratio (%)
Dechlorination	13.7	55.7	22.6	75.7	31.6	86.2
Inorganic chlorine	5.2	21.0	2.8	9.4	0.1	0.4
Organic chlorine	0.4	1.4	0.6	1.8	0.5	1.4
Unknown/Error	5.4	21.9	3.9	13.1	4.4	12.0
Total	24.7	100.0	29.9	100.0	36.6	100.0

### 5) Activation energy of heat decomposition

The activation energy of the heat decomposition is calculated. Fig. 3 shows Arrhenius plot for the time when the dechlorination of the original basic compound (M-2) becomes 50%. When the activation energy is calculated according to this Fig.3 , 62.2kJ/mol (14.8 kcal/mol) is obtained.

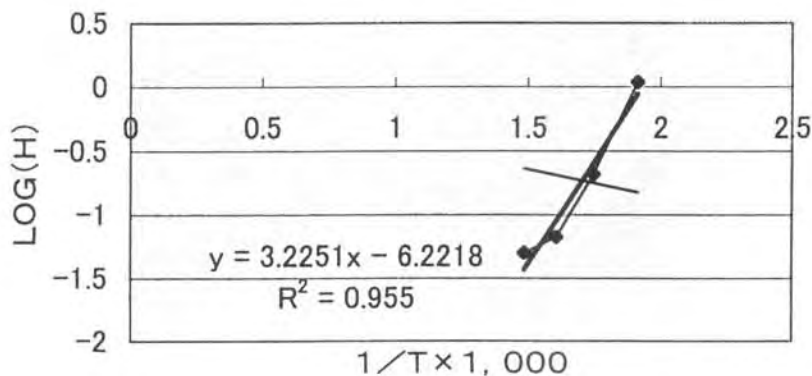


Fig. 3 Arrhenius plot of dechlorination reaction (M-2 compound)



#### 4. Summary

The behavior of the dechlorination of PVC was studied with its calcium carbonate compound amount varied. The findings through this study are as follows:

- ① Regardless of the calcium carbonate compound amount, the dechlorination reaction was not completed at a decomposition heat temperature of 250°C even after 80 min. have elapsed from the start of the heat decomposition. However, at the heat decomposition temperature of 300°C and higher, the dechlorination reaction is almost completed within about 20 min. after starting of the heat decomposition.
- ② The hydrogen chloride production rate of the original sample tends to decrease as the calcium carbonate compound amount increases. It is supposedly because the calcium carbonate reacts with the hydrogen chloride, changes into the calcium chloride and traps a part of the hydrogen chloride in the PVC.
- ③ It was not possible to identify a clear relationship between the hydrogen chloride production rate and calcium carbonate compound amount of the aged samples (10-year and 20-year). The reason can be explained as follows. The aged samples were pre-heated at 100 °C to promote the deterioration in advance. In this process, the dechlorination reaction was progressed slightly and reacts with the calcium carbonate. Then this causes the hydrogen chloride capturing capability of the calcium carbonate to lower.
- ④ The activation energy of the dechlorination reaction is 62.2kJ/mol (14.8 kcal/mol) in a temperature range of 250°C - 400°C.

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