Fundamental Study on Chlorination of Monazite

Isao TANABE, Shozo TAKASE and Hisao KONNO

Lab. of Azuma Kako & Co., Ltd., Fushiki-Kushioka, Takaoka, Toyama

1. Preface

Several reports were presented on direct chlorination of monazite, but details of which were not given of the condition and mechanism. The authors investigated the difference of reactivity of principal components and the conditions of chlorination upon monazite.

2. Difference of Reactivity of Principal Components

Theoretical quantity of charcoal was blended with either cerium oxide, lanthanum oxide, thorium oxide or monazite, respectively as shown in Table 1; and then, chlorination was performed under chlorine gas by raising temperature at the rate of 5°C/min., and the weight change was traced using thermo balance. Quantity of blended charcoal was calculated by assuming that reaction gas was CO alone and reaction product of phosphorus was PCl_5 alone. The results obtained are shown in Fig. 1 and the results indicate the following facts.

Table 1 Chemical Composition of the Specimens Used in the Experiment (Grain size : 325 mesh)

Kind of specimens	Composition (%)					
Monazite	R ₂ O ₃	58.1	ThO ₂	7.97	P ₂ O ₅	29.8
	Fe ₂ O ₃	0.32	SiO ₂	2.32		
Cerium oxide	CeO ₂	99.2				
Lanthanum oxide	La ₂ O ₃	99.5				
Thorium oxide	ThO ₂	98.9				
Charcoal	V.M.	11.3	Ash	2.2	F.C.	86.5
Artificial graphite	"	0.2	"	0.1	"	99.7

Notes. R : Rare earth, V.M. : Volatile matter,
F.C. : Fixed carbon

1. Cerium oxide
2. Lanthanum oxide
3. Thorium oxide
4. Monazite
5. Charcoal
6. Monazite (C free)

Fig. 1 Thermo-balance curve of chlorination

(1) The reaction of cerium oxide or lanthanum oxide began at 300~330°C or 280~290°C, respectively. Secondary abrupt increase of weight was observed at nearly 600°C in the both cases.

(2) The reaction of thorium began at about 400°C, and its extent increased with rising temperature; however, its weight decreased at higher temperature than 690°C due to the evaporation of thorium chloride produced.

(3) The reaction of monazite proceeds rather violently above 550°C, but it is difficult to indicate the beginning temperature of reactions by weight change only, since phosphorus contained may react with chlorine and the products may vaporize.

However, it is presumed that a part of rare earths changed into oxychloride at 250~500°C, considering from the curve of increasing weight of monazite and charcoal, and composition of reaction products at lower temperature.

(4) When charcoal was heated at 200~250°C in chlorine gas, the weight increase was seen. To clear up this cause, charcoal or graphite was heated up to 450°C gradually in chlorine current under the same condition, and weight increase, chlorine content and free chlorine of products were determined. The results are shown in Table 2. With a artificial a graphite containing no volatile matter very little weight increase was recognized. As a result of this experiment, it is considered that weight increases of charcoal is due to the reaction with chlorine; a part of hydrogen in charcoal was substituted by chlorine.

Table 2 Results Obtained by Heating of Charcoal and Artificial Graphite Powder in Chlorine Gas Using Thermo-balance (Max. temp. 450°C, rate of temp. rise 5°C/min.)

Specimens	Rate of weight increase %	Total Cl%	Free Cl%
Charcoal powder	10.3	9.4	tr.
Artificial graphite powder	0.1	0.1	tr.

3. Investigation of Reaction Conditions

Charcoal was blended with monazite and the mixture was moulded into briquette in size of 4~10 mm under pressure. Then chlorination was performed by using a quartz-boat in tube furnace to investigate reaction conditions. Scale of the experiment was as large as 20 g in briquette quantity.

3.1 Effect of reaction temperature Reaction time was fixed at 4 hours. The total quantity of chlorine gas was twice of the theoretical amount and adjusted to pass for 4 hrs., and the reaction temperature was investigated. The results obtained are shown in Table 3 and Fig. 2, and the results indicated the following facts.

Table 3 Relation Between the Temperature and the Composition of Reaction Products

Temp. °C	Composition wt. %						
	Insol. %	Insol. R	Sol. R	Insol. Th	Sol. Th	P	C
400	97.6	37.39	0.21	5.33	0	9.87	18.2
450	95.6	37.32	0.58	5.30	0	9.87	17.5
500	92.7	35.75	2.35	5.43	0	10.04	13.0
550	60.3	33.55	16.45	5.15	0.35	3.90	11.0
600	29.8	5.2	35.7	4.15	1.56	2.44	7.5
650	17.5	0.7	41.0	2.89	2.01	0.675	7.4
700	9.19	0.2	43.6	1.70	2.52	0.042	6.9
750	6.83	0.1	45.7	0.97	2.98	0.039	5.0
800	5.50	0	47.8	0.14	3.55	0.035	3.9
850	5.00	0	50.3	0.01	2.71	0.195	1.5
900	3.80	0.1	52.7	0	1.30	0.659	0.16
950	8.75	3.1	50.1	0.10	0.64	1.13	0.12
1000	22.3	11.3	42.4	0.01	0.19	2.00	0.10

Reaction 4 hrs.

(1) Chlorination of rare earths and phosphorus in monazite proceeded considerably at 550°C, and the reaction rate increased with rising temperature and reached the maximum at 700~850°C, but it decreased above 850°C which is the melting point of the reaction products. At higher temperature evaporation loss of rare earths was rather large.

(2) Reaction of thorium in monazite proceeded at higher temperature than that of rare earths or of phosphorus, and the reaction rate was almost the maximum at 800°C. Its reaction rate did not decrease at higher temperature such as 950~1000°C, and the separation was almost complete by evaporation.

Fig. 2 Relation among temperature and rates of reaction, and of evaporation of thoria and rare earth

3.2 Composition of products at low temperature Cerium oxide, lanthanum oxide or monazite were chlorinated. at low temperatures such as 400~450°C, and the existence of their oxychlorides in intermediate products were investigated. The results obtained are shown in Table 4. Waterinsoluble chlorides caused by the formation of oxychlorides was identified in the reaction products of cerium oxide at 400°C and monazite at 400°C, but not observed in the reaction product of lanthanum oxide at 400°C.

Table 4 Composition of Reaction Products at Temperature

Temp. °C	Composition wt. %					Charge and mixing ratio
	Insol.	Insol. R	Sol. R	Insol. Cl	Sol. Cl	
400	90.3	42.6	5.10	5.34	3.77	} CeO ₂ : Charcoal 86.1 : 13.9
450	59.5	20.5	22.9	2.43	17.47	
400	97.6	37.39	0.21	8.22	1.53	} Monazite : Charcoal 80.6 : 19.4
450	95.6	37.32	0.58	9.26	2.00	
400	32.4	16.7	37.4	0	28.3	La ₂ O ₃ : Charcoal 88.5 : 11.5

Reaction time : 4 hrs.

3.3 Effect of reaction time Temperature of chlorination upon monazite is classified into two groups; one is the temperature above the melting point of the product and the other is that below the melting point. Therefore, reaction time was investigated at 900°C and 700°C. The results obtained are shown in Table 5 and the following facts were classified.

Table 5 Relation Between Time and Reaction Rate

Temp. °C	Time hrs.	R		Th		P Rate of reaction %
		Rate of reaction %	Rate of evaporation %	Rate of reaction %	Rate of evaporation %	
700	1	91.0	3.4	28.5	3.1	78.1
"	2	94.6	2.0	60.1	18.3	85.1
"	4	99.5	3.5	78.4	20.5	99.6
900	1/2	72.1	11.0	55.7	48.9	71.9
"	1	77.6	16.1	72.4	68.8	82.2
"	2	97.9	10.2	94.8	83.7	95.5
"	4	99.9	12.5	100.0	85.8	95.8

(1) The reaction rates of rare earths and phosphorus were sufficiently high at 700°C for 4 hrs., while that of thoria was rather low.

(2) At 900°C, reaction rate of thoria was high, but the evaporation loss of rare earths was also high.

3.4 Composition of gas produced Gas produced by the reaction was gathered and the ratio of CO₂ to CO was investigated. The result obtained is shown in Fig. 3. The content of CO₂ was high in the product at low temperature, and it increased with proceeding reaction.

Fig. 3 Relation between time and gas composition

3.5 Composition of phosphorus chloride

Briquettes were directly set in a porcelain tube, and chlorination was performed on the scale of 200 g briquettes; then distilled phosphorus chlorides were gathered for fractional distillation. The results obtained by fractional distillation are shown in Table 6, and the results identified that phosphorus oxychloride was principal component and trichloride by-product.

Table 6 Result of Fractional Distillation of Condensate

Time hrs.		5	5	8
Rate of Cl ₂ volume per theoretical volume : %		91.2	91.2	172.0
P content of reaction product %		1.90	1.97	0.25
Rate of reaction of P %		83.5	83.2	98.9
Yield of distillate		56.0	50.0	74.7
Yield of fraction %	~102°C	15.4	10.1	11.9
	102~107°C	70.4	78.4	52.5
	residue	14.2	11.5	35.6

3.6 Effect of addition ratio of carbon Briquettes were made with several addition ratios of charcoal, and chlorination was performed at certain temperature below or above the melting point of the reaction products. The result obtained are shown in Table 7 and the results indicated that the addition ratio should be less than that of theoretical value below the melting point and be more than that of theoretical value at higher temperature than the melting point of the product.

Table 7 Relation Between Carbon Ratio and Reaction Rate

Temp. °C	Carbon ratio %	R		Th		P Rate of reaction %
		Rate of reaction %	Rate of evaporation %	Rate of reaction %	Rate of evaporation %	
750	100	99.7	3.8	93.0	33.2	99.7
"	90	99.8	3.1	92.8	33.5	99.7
"	85	99.2	3.3	92.2	34.3	99.7
"	80	98.5	2.9	92.0	35.2	99.5
"	75	95.5	2.5	92.5	35.7	98.3
1000	110	90.5	13.7	100.0	100.0	88.9
"	100	85.5	15.5	97.2	98.5	88.0
"	90	64.0	15.8	91.5	98.3	81.0

Reaction time : 4 hrs.

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Literature :

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