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Separation and Recovery of Rare Earth Elements from Phosphor Sludge of Waste Fluorescent Lamp by Pneumatic Classification and Sulfuric Acidic Leaching

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The pneumatic classification and acidic leaching behaviors of phosphor sludge have been examined to establish the recycling system of rare earth components contained in waste fluorescent lamp. At first, separation characteristic of rare earth components and calcium phosphate in phosphor sludge was investigated by pneumatic classification. After pneumatic classification of phosphor sludge, rare earth components were leached in various acidic solutions and sodium hydroxide solution. For recovery of soluble component in leaching solution, rare earth components were separated as hydroxide and oxalate precipitations. The experimental results obtained are summarized as follows:

(1) In classification process, rare earth components in phosphor sludge were concentrated to 29.3 % from 13.3 %, and its yield was 32.9 %.

(2) In leaching process, sulfuric acid solution was more effective one as a leaching solvent of rare earth component than other solutions. Y and Eu components in phosphor sludge were dissolved in sulfuric acid solution of 1.5 kmol/m^3, and other rare earth components were rarely dissolved in leaching solution. Leaching degrees of Y and Eu were respectively 92 % and 98 % in the following optimum leaching conditions; sulfuric acid concentration is 1.5 kmol/m^3, leaching temperature 343 K, leaching time 3.6 ks and pulp concentration 30 kg/m^3.

(3) Y and Eu components of phosphor sludge contained in waste fluorescent lamp were, effectively recovered by three processes of pneumatic classification, sulfuric acid leaching and oxalate precipitation methods. Their recovery was finally about 65 %, and its purity was 98.2 %.

Keywords: Fluorescent Lamp, Pneumatic Classification, Sulfuric Acid Leaching, Rare Earth Elements

1. Introduction

Rare earth components are commercially used as functional materials such as magnetic materials, optical glass, electronic and fluorescence materials (1). However, the rare earth components from the product are commercially not recycled up to date. There are some reports of recycling processes about braun tube used for color television (2), three wavelength fluorescent lamp (3) (4), the magnet scrap (5) and others. It is expected that the development of recycling technology will be required for the maintenance of resource and the relaxation of environmental problem, in future.

In general, the most of waste fluorescent lamp are treated by landfill. A few company are recently carrying out the separation treatment of phosphor sludge for the recovery of Hg in the fluorescent lamp (6). The glass and Hg are recovered from waste fluorescent lamp in the separation process (7). However, rare earth phosphor sludge are not entirely recycled, yet. The concentration process of rare earth phosphor is required to recover rare earth components efficiently, because waste fluorescent lamp is discarded as the mixtures of common lamp, three wavelength lamp, high color rendering lamp and others. The purpose of this research is to establish the concentration process of rare earth phosphor by pneumatic classification treatment and the recover process of rare earth components from phosphor sludge by sulfuric acid leaching method.

2. Experimental procedure

2.1 Sample

The separation process of waste fluorescent lamp in the mining company is classified as follows: (a) The waste fluorescent lamp is broken up in the crushing process. (b) The waste fluorescent lamp is separated into three parts of the

Table 1 Chemical analysis of phosphor sludge.

Elements	Na	Mg	Al	Si	P	Cl	Ca	Mn
mass(%)	0.29	0.14	0.13	1.1	15	0.44	35	1.0
Elements	Sr	Y	Sb	Ba	La	Ce	Eu	Tb
mass(%)	1.7	2.8	0.56	0.89	0.94	0.40	0.21	0.23

glass, the metal cap and the phosphor sludge. (c) The glass is cleaned to strip off the phosphor powder. (d) The phosphor sludge powder is calcined at high temperature for the removal of Hg. In this work, phosphor sludge collected in the crushing process was used as sample for pneumatic classification. As shown in Table 1, main components of phosphor sludge are Ca and P, and the contents of rare earth elements are 2.8 % for Y, 0.94 % for La, 0.40 % for Ce, 0.21 % for Eu and 0.23 % for Tb, respectively. Rare earth components consist of red, blue and green phosphors. The total content of rare earth phosphor is 13.3 %. From the SEM photograph of phosphor sludge, it was observed that each rare earth phosphor existed as single particle.

2.2 Pneumatic classification

Pneumatic classification was carried out by using the classification apparatus (model TC-25, Nissin Corp., Japan). The optimum conditions of pneumatic classification were adjusted by rotor velocity and air flow rate, and determined by evaluating both yield of fine powder and content of rare earth phosphor in fine powder.

2.3 Leaching

Phosphor sludge of rare earth components was leached in 18 kmol/m^3 H_2SO_4, 16 kmol/m^3 HNO_3, 12 kmol/m^3 HCl and 20 kmol/m^3 NaOH solutions, respectively. Various factors of acid concentration, time, temperature and pulp concentration were examined for determining the optimum leaching conditions. The sample of 10~10^{-3} kg was used in each leaching experiment, and it was stirred by a magnetic stirrer in leaching solution. The solid-liquid separation of the leaching solution was made by the filtration process. Rare earth elements in the leaching solution were chemically analyzed by ICP-AES (model 1200AR, Seiko Corp., Japan).

2.4 Removal of impurity component and recovery of rare earth component

At first, the impurity and rare earth components in the leaching solution were deposited as hydroxides by the addition of aqueous ammonia. Then, rare earth hydroxide was changed to oxalate by the addition of oxalic acid, and the impurity hydroxide was removed. Furthermore, Rare earth oxalate was calcined at 1173 K and recovered as a oxide. Rare earth oxide was analyzed by both of XRF and ICP-AES, and its purity was evaluated.

Table 2 Chemical analysis of phosphor sludge after pneumatic classification.

Elements	Na	Mg	Al	Si	P	Cl	Ca	Mn
mass(%)	0.39	0.26	1.4	1.8	13	0.48	29	0.75
Elements	Sr	Y	Sb	Ba	La	Ce	Eu	Tb
mass(%)	2.6	7.2	0.45	1.4	2.3	0.90	0.47	0.55

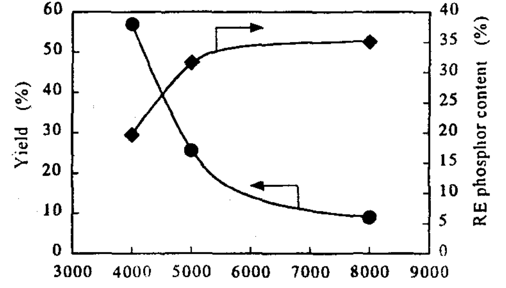

Fig.1 Effect of rotor velocity on yield and RE phosphor content of fine powder.(Air flow rate: 0.05 m^3/s)

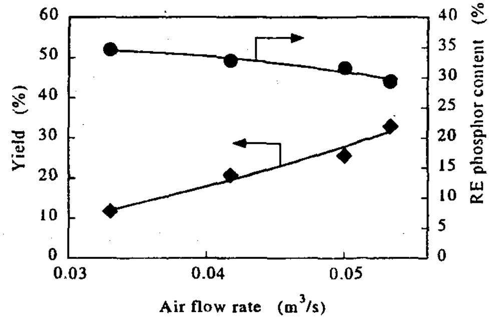

Fig.2 Effect of air flow rate on yield and RE phosphor content of fine powder.(Rotor velocity: 5000 r.p.m.)

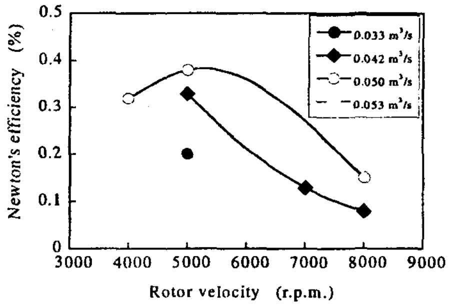

Fig.3 Relation between rotor velocity and Newton's efficiency at various air flow rates.

3. Results and Discussion

3.1 Separation of phosphor sludge by pneumatic classification

The relation between rotor velocity of pneumatic classification apparatus and yield of fine powder from phosphor sludge is shown in Fig.1. The relation between rotor veloc-

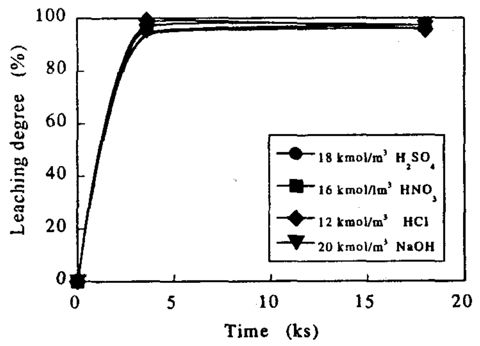

Fig.4 Relation between time and leaching degree of yttrium at various leaching solutions.(Temperature: 393 K, Pulp concentration: 100 kg/m³)

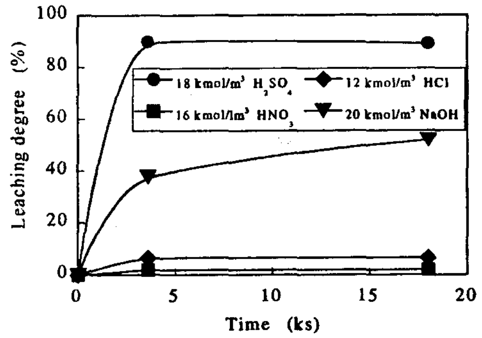

Fig.5 Relation between time and leaching degree of lanthanum at various leaching solutions.(Temperature: 393 K, Pulp concentration: 100 kg/m³)

ity and content of rare earth phosphor in fine powder is also shown in Fig.1. The effect of air flow rate on the yield of fine powder and content of rare earth phosphor in fine powder is shown in Fig.2. As shown in Fig.1, the content of rare earth phosphor increases with an increase in rotor velocity, and the yield of fine powder decreases with an increase in rotor velocity. Then, as shown in Fig.2, the content of rare earth phosphor give a constant value with increasing of air flow rate, and the yield of fine powder increases with increasing of air flow rate. The optimum conditions of pneumatic classification can be determined by using the Newton's efficiency, as shown in Fig.3. From the experimental results in Fig.3, the optimum conditions of pneumatic classification can be considered to be at rotor velocity of 5000 r.p.m. and at air flow rate of 0.053 m³/s

The chemical analysis of phosphor sludge after pneumatic classification under the optimum conditions is shown in Table 2. From these results, the yield of fine powder from phosphor sludge is 32.9 %, and the content of rare earth phosphor is found to be concentrated from 13.2 % to 29.7 %. The recovery degree of rare earth phosphor is 70 %, and the concentration ratio of phosphor sludge to fine powder is about 3.

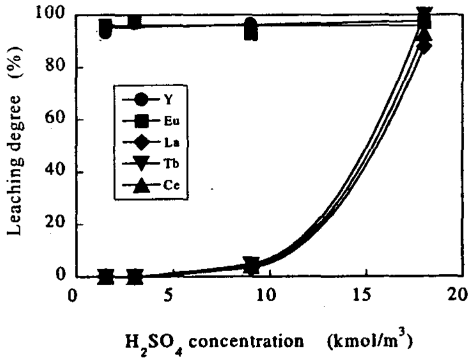

Fig.6 Effect of sulfuric acid concentration on leaching degrees of rare earth elements.(Time: 18 ks, Pulp concentration: 100 kg/m³, Temperature: 393 K)

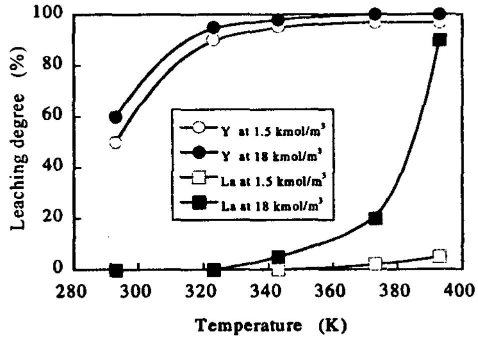

Fig.7 Effect of temperature on leaching degrees of yttrium and lanthanum at various H_2SO_4 concentrations.(Pulp concentration: 100 kg/m³, Time: 3.6 ks)

3.2 Leaching of phosphor sludge in various acidic solutions and NaOH solution

Rare earth phosphor sludge was leached in various mineral acidic solutions and NaOH solution. The effect of time on the leaching degrees of Y and La is shown in Figs.4 and 5. Leaching degree of Y is more than 90 % for 3.6 ks in each leaching solution. Leaching degree of La is 92 % in H_2SO_4 solution, 1.5 % in HNO_3 solution, 5 % in HCl solution and 50 % in NaOH solution.

Leaching residues in HNO_3 and HCl solutions were phosphate compounds. Therefore, Y existed in the form of oxide is considered to be easily dissolved in mineral acidic solution and NaOH solution, and La existed in the form of phosphate to be rarely dissolved in these solutions. High temperature treatment or the addition of oxidizing agent to the leaching solution may be required for the dissolution of La phosphate⁽⁸⁾. Then, sulfuric acid leaching may also be effective to separate each element of Ca, Sr and Ba from rare earth components, because these elements can be precipitated as sulfates.

Relation between sulfuric acid concentration and leaching degrees of rare earth components is shown in Fig.6. Leaching degrees of Y and Eu in sulfuric acid solution of 1.5 kmol/m³ are more than 90 %. The dissolutions of La, Ce

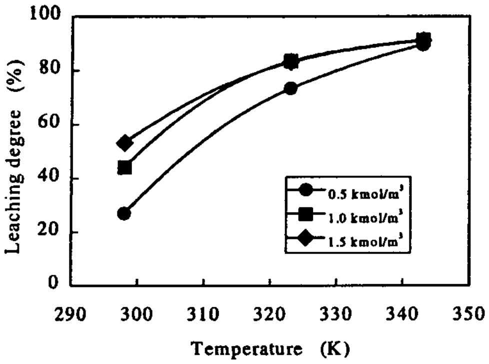

Fig.8 Effect of temperature on leaching degree of yttrium at various H_2SO_4 concentrations.(Time: 10.8 ks, Pulp concentration: 30 kg/m^3)

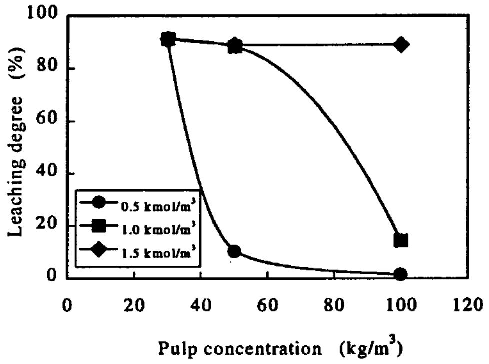

Fig.9 Effect of pulp concentration on leaching degree of yttrium at various H_2SO_4 concentrations.(Time: 10.8 ks, Temperature: 343 K)

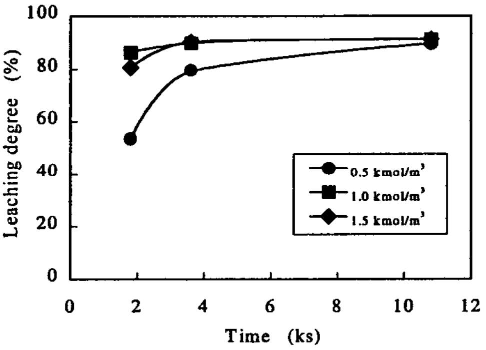

Fig.10 Effect of time on leaching degree of yttrium at various H_2SO_4 concentrations.(Pulp concentration: 30 kg/m^3, Temperature: 343 K)

and Tb are considered to proceed at above sulfuric acid concentration of 9 kmol/m^3, and their leaching degrees are more than 90 % in sulfuric acid solution of 18 kmol/m^3. The effect of temperature on the leaching degree of rare earth components is shown in Fig.7. Leaching degree of Y increases with rising of temperature in sulfuric acid solution, and is more than 50 % at 298 K and 90 % at 343 K. These experiment results are in fairly agreement with the leaching behavior of HCl solution reported in previous paper(9). La phosphor is not leached at temperature of below 323 K in sulfuric acid solution. The leaching reaction of La phosphor proceeds at 343 K in sulfuric acid solution of 18 kmol/m^3, and leaching degree of La is 20 % at 373 K and more than 90 %

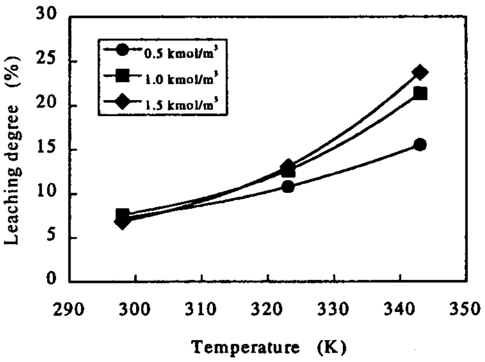

Fig.11 Relation between temperature and leaching degree of calcium at various H_2SO_4 concentrations.(Time: 10.8 ks, Pulp concentration: 30 kg/m^3)

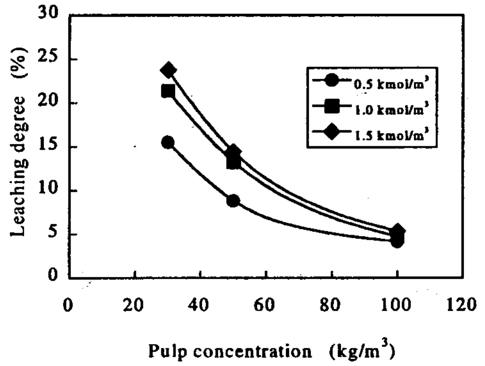

Fig.12 Relation between pulp concentration and leaching degree of calcium at various H_2SO_4 concentrations.(Time: 10.8 ks, Temperature: 343 K)

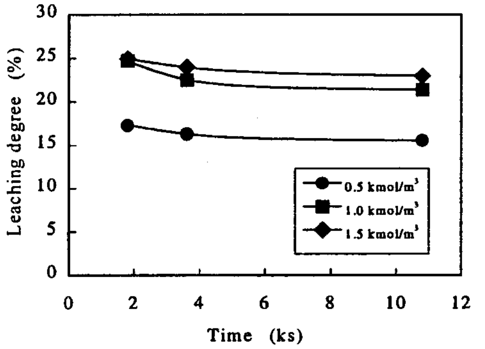

Fig.13 Relation between time and leaching degree of calcium at various H_2SO_4 concentrations.(Pulp concentration: 30 kg/m^3, Temperature: 343 K)

at 393 K. Moreover, it is also suggested from Fig.7 that the leaching reaction of La phosphor begin at 373 K in sulfuric solution of 1.5 kmol/m^3, and its leaching degree is 5 % at 393 K. In sulfuric acid leaching, the dissolution behavior of Y phosphor is different from that of La phosphor, because Y compound exists in the form of oxide and La compound exists in the form of phosphate. Therefore, separation of Y and Eu phosphors and La, Ce and Tb phosphors is considered to be possible in sulfuric acid leaching.

On the basis of these experiment results, the leaching experiment of Y and Eu from phosphor sludge concentrated by pneumatic classification was carried out in sulfuric acid solution. Effects of leaching temperature, time, and pulp concentration on leaching degree of Y are shown in Figs.8, 9 and 10. It is suggested from Fig.8 that leaching degree of Y is more than 90 % at temperature of above 343 K. When phosphor sludge is treated by using the amount of below 30 kg in leaching solution of 1 m^3, leaching degree of Y is 90 % in sulfuric acid solution of 0.5 $kmol/m^3$. When rare earth phosphor sludges of 100 kg and 150 kg are leached in sulfuric acid solution of 1.0 $kmol/m^3$ and 1.5 $kmol/m^3$, leaching degree of Y is 90 % at temperature of 343 K for 3.6 ks. As shown in Fig.10, leaching degree of Y in various sulfuric acid solutions increases with an increases in time and is 90 % at 343 K for 10.8 ks.

Furthermore, the leaching behavior of Ca phosphate which is one of main constituents in phosphor sludge was examined. Effects of leaching temperature, time and pulp concentration on leaching degree of Ca are shown in Figs.11, 12 and 13. Leaching degree of Ca increases with raising the temperature and decreasing the pulp concentration. Leaching degree of Ca shows a constant value for a short time. Though calcium halo phosphate is dissolved in sulfuric acid solution, the dissolved Ca ion at once reacts with sulfuric acid and precipitates as calcium sulfate. Therefore, the leaching behavior of Ca phosphate in phosphor sludge is controlled by a solubility of the formed calcium sulfate. The solubility of calcium sulfate in sulfuric acid solution is 2.7 kg/m^3 at 298 K and 3.8 kg/m^3 at 316 K, and increases with the rise of temperature. Then, Ca content in leaching solution become a constant value because the solubility of Ca is constant in the same conditions.

According to the results mentioned above, the optimum leaching conditions for rare earth components are as follows; sulfuric acid concentration is 1.5 $kmol/m^3$, pulp concentration 30 kg/m^3, leaching temperature 343 K and leaching time 10.8 Ks. The leaching degrees of Y and Eu components were respectively 92 % and 98 % under the optimum conditions.

3.3 Removal of impurity component and recovery of rare earth component

Leaching degrees of various elements shown in Table 1 were chemically analyzed to examine impurity concentration in the leaching solution. Leaching degrees of Ba, Sr and Si were below 5 % and that of Ca was 24 %. Leaching degrees of other elements were above 90 % under the optimum leaching conditions. Ba, Sr and a part of Ca in sulfuric acid solution were precipitated in the form of slightly soluble sulfate. Si was also precipitated in the form of insoluble silicate in sulfuric acid solution. These elements could be eliminated by solid-liquid separation process after sulfuric acid leaching. From these results, it was understood that the impurity components in the leaching solution were considered to be each one of Ca, Na, P, Cl, Mg, Sb, Mn and Al. When the ammonia water of six times the molar quantity of rare earth elements was added into the leaching solution, both of hydroxides of rare earth and impurity elements were precipitated in the neighborhood of about pH 10. After solid-liquid separation of the precipitates, they were also dissolved with hydrochloric acid solution. It was confirmed from the chemical analysis results of elements in hydrochloric acid solution that each element of Na, P, Cl, Ca and Mg was removed in hydrochloric acid solution. Both of Y and Eu hydroxides were formed at beyond pH 5, and its precipitation was stable at the pH range of the strong alkali area. Each element of Na, P and Cl was not precipitated as hydroxide, and both of Ca and Mg were not precipitated as hydroxides at the weak alkali area of pH 10. It was possible that these impurity elements were removed from the mixed solution of Y and Eu in the range from pH 5 to pH 10.

When oxalic acid of three times the molar quantity of rare earth elements was added into HCl solution after the dissolution of hydroxide precipitation, Y and Eu oxalate compounds were formed. Impurity elements of Sb, Mn and Al did not form the oxalate compounds in this process. Therefore, Y and Eu oxalate compounds were calcined at 1173 K,

Table 3 Chemical composition of rare earth oxide recovered.

Elements	Y_2O_3	Eu_2O_3	La_2O_3	CeO_2	Tb_4O_7
mass(%)	93	6.0	0.11	0.10	0.1>
Elements	Al_2O_3	SiO_2	SO_3	CaO	SrO
mass(%)	0.1>	0.1>	0.1>	0.51	0.12

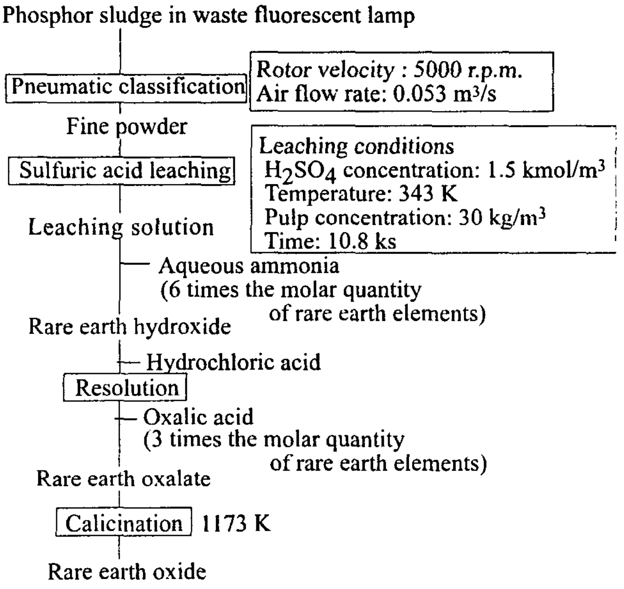

Fig.14 Flow sheet for recoveries of yttrium and europium oxides.

and rare earth oxides could be synthesized. The chemical analysis values of rare earth oxide are shown in Table 3. Though both of Ca and Sr are slightly contained as impurities in these oxides, the purity of rare earth oxide is beyond 99 %.

3.4 Recycling process of phosphor sludge

Separation and recovery flow of rare earth components from phosphor sludge could be established on the base of the experimental results mentioned above. The flow sheet is shown in Fig.14.

The pneumatic classification was carried out by using phosphor sludge of 10 kg in accordance with the treatment process of Fig.14. In this exprements, the chemical composition of phosphor sludge after pneumatic classification was almost equal to the chemical analysis value given in Table 2. The large leaching apparatus in capacity was made of stainless steel, and sulfuric acid leaching experiment was performed under the optimum conditions determined previously. Leaching degrees of Y and Eu components were more than 90 % for the leaching time of 1.8 ks. Next, the impurity removal and recovery of rare earth components were carried out in accordance with the flow sheet, and rare earth oxide was finally synthesized. The purity of rare earth oxide synthesized was 98.2 %. The purity of product did not become above 99 % because both of Ca and Sr could not be entirely removed by the increase of treatment amount.

In above experiment, recovery degree of rare earth phosphor was 70 % in pneumatic classification process, and leaching degrees of Y and Eu components were 93 % and 95 % in sulfuric acid leaching process, respectively. The recovery degrees of Y and Eu components from phosphor sludge was calculated to be 65 % for Y and 67 % in the whole process.

4. Conclusions

The pneumatic classification and acidic leaching behaviors of phosphor sludge have been examined to establish the recycling system of rare earth components in waste fluorescent lamp. The experimental results obtained are summarized as follows:

(1) Waste phosphor sludge consisted of rare earth phosphor of 13.3 %.

(2) After pneumatic classification under the optimum conditions, the yield of fine powder was 32.9 %, and rare earth phosphor was concentrated from 13.2 % to 29.7 %. Recovery degree of rare earth phosphor was 70 %, and concentration ratio of phosphor sludge to fine powder is about 3.

(3) In leaching process, sulfuric acidic solution was more effective one as a leaching solvent of rare earth components than other solutions. Both of Y and Eu components contained in phosphor sludge were dissolved in sulfuric acid solution of 1.5 kmol/m^3, and other rare earth components were rarely dissolved in leaching solution. Leaching degrees of Y and Eu components were 92 % and 98 % in the following optimum leaching conditions; sulfuric acid concentration is 1.5 kmol/m^3, leaching temperature 343 K, leaching time 3.6 ks and pulp concentration 30 kg/m^3.

(4) In recovery process, Y and Eu components could be recovered to above 99.1 % by means of hydroxide treatment and oxalate precipitation method.

(5) Recovery process of rare earth components from phosphor sludge was established. According to the treatment process carried out by using phosphor sludge of 10 kg, Y and Eu components of phosphor sludge contained in waste fluorescent lamp could be recovered effectively by three treatment processes of pneumatic classification, sulfuric acid leaching and oxalate precipitation. Their recovery was finally about 65 %, and its purity was 98.2 %.

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