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Dissertation Summary

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SUMMARY

Optical Characterization and Recovery of Valuable Matter from Industrial Wastes Towards Functional Materials

Zero waste strategy is introduced to industries in order to maximize recycling, minimize waste, and ensure waste materials. The strategy brings the possibility that the waste materials are returned to functional materials in industrial system. The impact of the strategy goes to contribution of waste sectors to industrial re-design from one-way system into circular industrial system. This system is known as an industrial ecology or industrial recycling networks for waste exchange. However, many industries remain in one-way system due to lack of investigation dealing with valuable matter-containing wastes, for example wasted shells from pearl oyster farming/industries in Uwajima city, Ehime prefecture, Japan. Lack of investigation of the wasted shells results in lack of chance to promote them into waste exchange networks in recycling industries. Another example is rare earth elements contained in glass-polishing sludge. Glass particles from glass-polishing sludge contain rare earth elements originated from optical glasses. Investigations of glass-polishing sludge mainly focus on recovery of cerium. Most studies have tended to focus on recovery of cerium while no one, to the best of our knowledge, has studied recovery of rare earth elements-containing glass particles from glass-polishing sludge. This condition brings about rare earth elements contained in glass particles remain unrecovered. Thus, intensive studies of these industrial wastes are necessary to provide many recovery and recycling alternatives. In addition, industrial waste studies assist the development of industrial recycling networks.

The main objectives of this thesis are to characterize wasted shell, *Pinctada vulgaris* from pearl oyster farming in the Uwajima city and recovery of rare earth elements from glass-polishing sludge. This thesis consists of four chapters as follows:

In chapter 1, background, previous studies and objectives of the present study were summarized.

In chapter 2, optical characterization of fluorescent matter from wasted shell of *Pinctada vulgaris* shells was described. The purpose of this work is to characterize fluorescent matter and its distribution, presence of organic substances, composition, and elements composed the prismatic layers of *Pinctada vulgaris* shell. Fluorescent matter occupies only at the outer part of the shell namely prismatic layers. Microstructure of prismatic layers is dominated by calcite (CaCO_3) with vertical organic membranes and growth lines transecting the organic membranes. Organic substances are present in prismatic layers as appear in weight loss and exothermic reactions of TG-DTA curve of powdered prismatic layers. It is estimated 7.1 wt% organic substances in prismatic layers. The fluorescent matter might be originated from these organic substances and it forms black-red lamellar pattern under UV irradiation in the cross section of prismatic layers. Observation using fluorescence micro spectroscope revealed that the black-red fluorescent lamellar pattern was due to emission intensity modulation and correspond to sulphur element concentration. Excitation and emission spectra of prismatic layers both powder and extracted liquid show similarity to that of synthetic uroporphyrin. Porphyrins are recognized as fluorophores with high intense fluorescence because have extensive system of electron transitions called Soret band (380–500 nm) and Q-bands (500–750 nm). Acid base extraction was applied to obtain extracted liquid from prismatic layers. Prior to extraction, prismatic layers showing red fluorescence were selectively picked up under UV LED. This method promotes high concentrated fluorescent matter obtained from the extraction process. Features of porphyrin spectra are well agree with the spectra of extracted liquid. This suggests extraction process are suitable for that organic substances containing porphyrin derivatives.

In chapter 3, the effect of P_2O_5 addition on recovery of rare earth elements from glass particles-containing glass-polishing sludge was examined. The objective of this work is to recover europium from simulated glass particles by P_2O_5 addition. Recovery of rare earth from glass particles-containing glass-polishing sludge was conducted by melting with P_2O_5 addition and then leaching with water. Our previous experiments successfully revealed the composition condition of P_2O_5 to coordinate with rare earth ions in phospho-silicate glass system. Glass particles-containing glass-polishing sludge is considered as a multi-component glass system. Therefore, glass cullet was used as simulated glass particles because it has multi-components namely SiO_2 , Al_2O_3 , Na_2O , MgO , CaO , K_2O . By melting with P_2O_5 , it is postulated that rare earth elements coordinate with phosphate in simulated glass particles. Due to P_2O_5 addition, however, glass samples became lack of transparency. For that reason, europium was selected as dopant in glass cullet and utilized its fluorescence spectra for the estimation of local structure around europium ions. structural analysis. In the fluorescence spectra, europium has the forced electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition band, which is hypersensitive to glass composition, and the allowed magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition band, which is independent from glass composition. Ratio between these two transition bands called fluorescence intensity ratio, I-ratio = $I(^5\text{D}_0 \rightarrow ^7\text{F}_2) / I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ was suitable to estimate local vicinity of Eu^{3+} ions, whether Eu-O-A or Eu-O-P coordination (A: alkali and alkaline earth metals). I-ratio of simple glass systems: silicate, phosphate and phospho silicate glasses doped with europium ions were obtained. From this result, it is estimated that Eu -doped silicate glasses have Eu-O-A coordination, whereas Eu -doped phosphate and Eu -doped phospho silicate glasses have Eu-O-P coordination. In a simulated glass particle sample (cullet+ Eu), I-ratio of this glass is nearly equal to that of a simple silicate glass system which indicates europium ion

coordination in silicate networks of cullet+Eu glass is Eu–O–A (A : alkali-alkaline earth metals). This estimation was based on the fluorescence intensity of hypersensitive transition band. In silicate glass, intensity of hypersensitive bands increases with increasing ionic radius of modifier ions in the order of $\text{Li} < \text{Na} < \text{K}$. This increase is likely due to modifier ion sits in the second neighbor ion (Eu–O–A). In phosphate and phospho-silicate glasses, the intensity of hypersensitive bands was independent of ionic radius of modifier ions. This condition brings to estimation that phosphorus sits in the second neighbor ion to form Eu–O–P bonding.

Addition of P_2O_5 to the glass cullet system changed glass structure from silicate networks to phospho-silicate networks. When phosphate was added into the glass cullet, phosphate with the alkali-alkaline earth metals in glass cullet would form PO_4 networks: orthophosphate, pyrophosphate, and/or metaphosphate. The changes also affect europium ion coordination in the glass networks. To analyze effect of structural change to europium ion coordination, alkali-alkaline earth metals to phosphate ratio, A/P-ratio, was considered to affect the I-ratio of (cullet+Eu)- $x\text{P}_2\text{O}_5$ glass (x : P_2O_5 composition in mol%). The effect of P_2O_5 addition to I-ratio of (cullet+Eu)- $x\text{P}_2\text{O}_5$ glass was found into two conditions: A/P ratio > 1 and A/P ratio ≤ 1 . I-ratio of (cullet+Eu)- $x\text{P}_2\text{O}_5$ glass in the condition A/P ratio > 1 are comparable to the simple silicate glass system. Meanwhile, I-ratios of (cullet+Eu)- $x\text{P}_2\text{O}_5$ glass in the condition A/P ratio ≤ 1 are similar to those of phospho-silicate glasses indicating europium ion coordination is Eu–O–P.

IR spectra of (cullet+Eu)- $x\text{P}_2\text{O}_5$ glasses indicate the presence of metaphosphate (Q^2) chains at A/P ratio ≤ 1 such as (cullet+Eu)- $45\text{P}_2\text{O}_5$. Presence of the metaphosphate chains increases with increasing phosphate content indicated by increasing absorption intensity at $1200\text{--}1260\text{ cm}^{-1}$. Since metaphosphate chains and Eu–O–P coordination are present in the same condition, A/P ratio ≤ 1 , it is estimated that doubly bonded oxygen (P=O) in metaphosphate chains coordinate with significant amount of Eu^{3+} ions. The metaphosphate chains in this condition might promote recovery efficiency of europium due to their high solubility in water. Therefore, recovery of europium becomes more efficient with increasing concentration of P_2O_5 addition. At A/P-ratio = 0.34, recovery efficiency achieved 100% due to domination of metaphosphate chain as indicated by high intense absorption band of IR spectra.

In chapter 4, conclusions of finding in every chapter are summarized.

Pinctada vulgaris shells are of wasted shells in pearl oyster farming in the Uwajima city. It is found that the shell contains approximately 7.1 wt% organic substances in its prismatic layers. The organic substances have porphyrin derivatives that show black-red fluorescence forming lamellar pattern in prismatic layers under UV irradiation. The fluorescent matter can be extracted by acid base extraction. Further investigations are necessary to explore deeply about the fluorescent matter distribution in prismatic layers. The lamellar fluorescence distribution might be an indication of certain condition of the pearl oyster during growth period for example, sea environment and climate change, metabolism of the pearl oyster and quality level of the pearl in the shell. Our finding is one-step for the next findings that correspond this fluorescent distribution with a certain condition of pearl oyster. We believe our investigation will assist the development of pearl oyster farming/industries.

Recovery of europium from glass cullet as simulated glass particles-containing glass-polishing sludge was conducted by melting with P_2O_5 addition, then leaching with water. Important condition to consider for obtaining high recovery efficiency of europium is alkali-alkaline earth metal to phosphate ratio, A/P-ratio. A/P-ratio ≤ 1 is good condition for europium ions to coordinate with phosphorus (Eu–O–P) in the form metaphosphate

(Q²) chains. If metaphosphate (Q²) chains become dominant due to P₂O₅ addition, it will attract significant amount of europium and recovery efficiency of europium may achieve ~100% dissolved in water. For further studies, it is needed to consider recovery process of rare earth elements coupled with recycling process of P₂O₅ since raw material of phosphate are finite resources. Most interesting point for continuing this research is to utilize phospho-silicate system as a trapping agent for rare earth elements in rare earth elements-containing industrial wastes. The trapping agent is expected to concentrate and separate rare earth elements in a certain phase of slag system. This condition will promote high efficiency of recycling process.