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Studies on Coprecipited Phases in the Calcium-Gadolinium Oxalate System

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Calcium oxalate is often used as a carrier for precipitating rare earth elements. Gadolinium was chosen as a rare earth element and X-ray powder diffractometry used for the identification of coprecipitated solids. The X-ray lattice spacings are tabulated for each of the coprecipitates of varying composition in the calcium-gadolinium oxalate system. From the spacings, the following facts were obtained: (1) The uptake mechanisms of gadolinium in calcium oxalate, and calcium in gadolinium oxalate are completely due to the formation of solid solutions. (2) Several new solid solution phases were formed. (3) When the gadolinium to calcium ratio is proper, precipitates having a weddellite structure, which is not obtained in usual analytical procedures, are formed.

The purpose of the present work is to show that the various forms of the hydrated calcium-gadolinium oxalate system can be built up from a trace amount to a large percentage of gadolinium ions in aqueous solutions, with emphasis laid on the fact that some of the unstable forms of hydrated calcium oxalate may be stabilized by the addition and intervention of the tripositive gadolinium ions.

It is well-known that calcium oxalate is often used as a good carrier to precipitate the rare earth elements and other elements. Among these may be mentioned the separation of rare earth elements from uranium, beryllium, aluminum and zirconium by simply agitating an acetic acid solution of the mixture with solid calcium oxalate monohydrate. A similar technique has been used to separate the rare earth elements and strontium from zirconium, niobium and ruthenium.[1-3]

Following an intensive study of the coprecipitation of rare earth elements with various calcium oxalate hydrates, it has been found that calcium oxalate dihydrate carries small amounts of rare earth elements through mixed crystal formation and that the uptake of rare earth elements by calcium monohydrate follows the Freundlich adsorption isotherm.[1] In the case of thorium, calcium oxalate trihydrate

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[1] B. C. Purkayastha and S. N. Bhattacharyya, *J. Inorg. Nucl. Chem.*, **10**, 103 (1959).

[2] B. C. Purkayastha and S. N. Bhattacharyya, *J. Indian Chem. Soc.*, **41**, 71 (1964).

[3] T. Shigematsu, M. Tabushi and M. Matsui, *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 381 (1962).

does not take up thorium by way of mixed crystal formation, while dihydrate does.[2]

It was reported that the coprecipitation of a number of elements with calcium oxalate followed the logarithmic distribution law, and that some discrepancies existed in such systems as yttrium-calcium oxalates and scandium-calcium oxalates.[4] The former followed the logarithmic distribution law through a wide range of pH, while the latter obeyed the same law only below pH 3.5, and deviated gradually with increase in pH until pH 4 was reached, after which the system followed the homogeneous distribution law entirely.[3]

From the investigations cited above, it is obvious that the processes of coprecipitation are essentially affected by the forms of calcium oxalate crystals. A number of studies on the crystal forms of hydrated calcium oxalate are found in the literature.[5-7] Those on the phase diagrams and thermodynamic properties[8] have also been reported. For the most part of them, the description and identification of these crystalline species were given in terms of thermogravimetry, X-ray powder diffractometry and infrared spectrophotometry.

The conclusion may be drawn from the results of the above studies, that among various hydrates of calcium oxalate, the most stable one at room temperature is the monohydrate,[5] and the more unstable forms are the dihydrate, the trihydrates and the intermediate hydrates with nonintegral numbers of water molecules between two and three.[6] Some authors designated the monohydrate as form A, and the trihydrates as forms B, C, and D.[5,9] However, more proper names from mineralogy of whewellite[10] for form A and weddellite[11] for form B may be adopted in the investigation of the crystal structures.

Although the formation of solid solutions of trace amounts of rare earth elements with calcium oxalate has been studied by several groups of workers in recent years, little attention was paid to the study of precipitated phases of the calcium-rare earth element oxalate system when the percentage of rare earth element became high. On the other hand, many studies have been made on the phase relations by thermolysis between one hydrate and another, as well as between two forms of the anhydrous salt of calcium oxalate.[7,8,12] Nevertheless, investigations along these lines were scarcely extended beyond detailed information as to whether or not the phases of the calcium oxalate hydrates may have tendency to be changed or stabilized by other cations of similar size.

Experimental

Reagents. Gadolinium nitrate solution was prepared from 99.9% Gd_2O_3, supplied by Miyazaki Chemical Co., Tokyo, Japan. Calcium nitrate solution was prepared from the special grade (JIS) calcium carbonate. Concentrations of these solutions were determined by titration with standard EDTA solution.

Apparatus. All X-ray measurements were carried out with a Rigaku-Denki "Geigerflex" X-ray difractometer, and operated throughout this investigation at 30 kV and 15 mA, using a copper target.

Procedure. For the most of the data in this paper, a total of 200 m*l* of the solution containing about 3 mM of total ions was prepared as nitrate. Methyl red was used as an indicator, and a few drops of dilute ammonium hydroxide and then dilute nitric acid were added until the color just changed from yellow to pink. Most of the experiments were performed at the room temperature around 30°C.

To the above solution was added, with vigorous stirring, 50 m*l* of reagent solution containing 2 g of ammonium oxalate, sufficient to precipitate both the gadolinium and the calcium ions. The turbid mixture was allowed to settle over-night. Precipitated oxalates were collected on filter paper, and washed with a small amount of 0.5% ammonium oxalate, and then with deionized water.

The precipitation from hot solutions was made in the same manner as described above, except that the solutions containing calcium and gadolinium ions were heated to boil, and then hot solutions containing the ammonium oxalate were poured with vigorous stirring. Rapid precipitation set in almost immediately, and was usually completed within a few minutes.

Results

Since the main purpose of this experiment is to determine the forms of phases of the precipitates by means of X-ray powder diffraction, the d-spacings of the precipitates have been carefully compared with those of whewellite[10] and of weddellite.[11] The results are summarized and compiled in two tables.

(1) Precipitates prepared at room temperature

The precipitates containing 0—1 atomic % of gadolinium formed at room temperature consist of fine crystals with the characteristic spacings of whewellite. When the gadolinium content exceeds 2%, the precipitates no longer show whewellite-like structure, but exhibit the characteristic spacings of weddellite until the atomic percentage of gadolinium increases up to 30. The sharp contrast is readily seen in Table 1. For convenience, the two phases consisting of whewellite-like and weddellite-like

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[4] T. Shigematsu, M. Tabushi and M. Matsui, This Bulletin, **37**, 1610 (1964).

[5] J. Lecomte, T. Pobeguin and J. Wyart, *J. Phys. Radium*, **6**, 22 (1945).

[6] L. Walter-Levy and J. Laniepce, *Compt. Rend.*, **254**, 1073 (1962).

[7] P. L. Waters, *Nature*, **178**, 324 (1956).

[8] N. Gerard and G. Watelle-Marion, *Compt. Rend.*, **261**, 2363 (1965).

[9] Fink, Inorganic Index to the Powder Diffraction File, **14**, 768—771, ASTM Publication (1965).

[10] A. J. Gude, 3rd, E. J. Young, V. C. Kennedy and L. B. Riley, *Am. Mineralogist*, **45**, 1257 (1960).

[11] C. O. Hutton and W. H. Taft, *Mineral. Mag.*, **34** (268), 256 (1965).

[12] H. J. Arnott, F. G. E. Pautard and H. Steinfink, *Nature*, **208**, 1197 (1965).

Table 1. X-Ray powder diffraction data for Ca and Gd oxalate precipitated at room temperature (Cu$K\alpha$, λ=1.5418 Å)

Whewellite		Weddellite		Spacing	Atomic % of gadolinium										Phase
d(Å)	I	d(Å)	I	d(Å)	0	0.3	1	2	5	15	30	70	85	100	
				7.90										24	G
				7.63									100		γ
				7.56								86		53	γ, G
				7.53							17				γ
				7.50						24					γ
				6.24					16	11	9	4	4		β, γ
		6.17	90	6.22				16							β
5.95	75			5.97	11	12	13								α
5.79	27			5.83	6	4	4								α
				5.75								5	6		γ
				5.74						3	5				γ
				4.93										3	G
				4.80								4	4		γ
				4.79						3	5				γ
		4.40	60	4.44				7	8	4	2				β
				4.35									3	3	γ, G
				4.34						2	2	2			γ
				3.92										7	G
				3.91									4		G
				3.90							3	3			γ
				3.75								6	7		γ
				3.74						3	2				γ
3.63	100			3.66	30	13	12								α
				3.45									2	2	γ, G
				3.21						2	2	2	2	1	γ, G
		3.09	40	3.10				3	4	3	3	2			β
		2.82	10	2.83				5	5	3	2	2	2		β, γ
		2.77	100	2.79				12	16	11	5				β
				2.47								2	3		γ
				2.46							2				γ
		2.42	40	2.43				3	3	3	1				β
		2.40	40	2.41				5	5	3	2				β
				2.38							2	2	3	1	γ, G
2.36	68			2.37	11	7	6								α
		2.24	70	2.25				7	8	4	2				β
2.21	10	2.21	20	2.21	1	1	1	2	3	2	2				α, β
		2.12	50	2.12				2	3	2	1				β
				2.11										2	G
				2.10							2	2	3		γ

structures are respectively designated as α and β forms of the Ca-Gd oxalate system.

As the gadolinium content attained a range of between 30 and 85% in the solution, the coprecipitated phases give diffraction patterns with entirely different spacings, comprising 4.80, 3.90, 3.21, 2.46, 2.38, 2.10 A, *etc.* These are designated as the γ form so as to be distinguishable from the other forms. It is noteworthy that the values of the d-spacings for any form stated above do not vary over a wide range of composition.

Pure hydrated calcium oxalate and pure hydrated gadolinium oxalate were also prepared by the same method as described in the paragraph under the heading of " Procedure." The former is a typical artificial whewellite, and is distinctly recognizable from its characteristic spacings. The latter is not known in nature, and the name " G form " is given to this solid phase that has spacings of 7.56, 4.93, 4.35, 3.92, 3.45 A, *etc.* Among these, the 7.56 A spacing gives the strongest diffraction.

(2) Precipitates prepared at elevated temperature

The results are quite different when the coprecipitation was carried out at an elevated temperature. The precipitates thus obtained with amounts of

Table 2. X-ray powder diffraction data for Ca and Gd Oxalate precipitated at elevated temperature (Cu$K\alpha$, λ=1.5418 Å)

Whewellite		Spacing	Atomic% of gadolinium							Phase
d(Å)	I	d(Å)	0	10	30	50	70	85	100	
		6.17							100	G′
		6.09						33		δ
		6.07					29			δ
		6.01			51	32				α, δ
		5.99		63						α
5.95	75	5.95	59							α
		4.84							15	G′
		4.80			4	3	6	10		δ
		4.32							33	G′
		4.30					4	7		δ
3.63	100	3.65	55	45	40	27	28	11		α, δ
		3.13							11	G′
		3.12						4		δ
		3.11					4			δ
		3.04							8	G′
		3.03					10	9		δ
		3.02							10	G′
		2.98		31	29	19	17	9		α
2.97	100	2.97	31							α
		2.92		11	9	7	7	6	12	α, δ, G′
2.90	18	2.91	10							α
		2.52				4	5	6	7	δ, G′
		2.51						5		δ
2.49	35	2.50	12	9	8	7	7			α, δ
		2.45						7	15	δ, G′
		2.44						7		δ
2.36	68	2.36	31	21	19	15	13	11		α, δ
		2.34							15	G′
2.25	25	2.26	9	7	5	5				α
		2.15						5	10	δ, G′
		2.12							7	G′
		2.09						5		δ
2.07	21	2.08	9	4	5	7	5			α, δ
		1.99							7	G′
1.98	20	1.98	8	7	7	6	7	7		α, δ
		1.96						5		δ
1.95	16	1.95	7	7	10	7	5			α, δ
1.93	22	1.93	7	7	5	3				
		1.83							12	G′
1.81	13	1.82	7	5	5	4	6	7		α, δ

gadolinium varying from traces to a very large percentage are identified as fine crystals with characteristic spacings of whewellite, the α form according to our designation. No weddellite-like structure (β form) is found.

Pure hydrated gadolinium oxalate was also prepared. At temperatures around 100°C, a lower hydrate rather than a higher hydrate is formed. Its spacings are remarkably different from those of the G form, hence the name of G′ form is given to this phase. From solutions of high concentrations of gadolinium, still another phase appeared, which gave weak diffraction patterns. This phase is designated as the δ form. The various forms obtained from the solutions at the elevated temperature are summarized in Table 2.

Discussion

From the experimental results, proper formulas can be used to depict the various forms of the hydrated calcium and gadolinium oxalates which were precipitated in the respective solutions either at room temperature or at elevated temperatures.

TABLE 3. FORMULAS SUGGESTED FOR THE HYDRATED Ca-Gd OXALATES PRECIPITATED AT ROOM TEMPERATURE*

Form of phase	Formula
α	$(Ca_{1-x}, Gd_{2x/3})(COO)_2 \cdot H_2O$
β	$(Ca_{1-x}, Gd_{2x/3})(COO)_2 \cdot 2H_2O$*
γ	$(Gd_{1-x}, Ca_{3x/2})_3(COO)_3 \cdot mH_2O$
G	$(Gd_{1-x}, Ca_{3x/2})_2(COO)_3 \cdot nH_2O$

* The formula for the β form may be also expressed as

$$(Ca_{1-x}, Gd_{2x/3})(COO)_2 \cdot (2+y)H_2O$$

in which y has a value varying between 0 and 0.5. The fractional portion of the H_2O content is zeolitic.

TABLE 4. FORMULAS SUGGESTED FOR THE HYDRATED Ca-Gd OXALATES PRECIPITATED AT ELEVATED TEMPERATURES

Form of phase	Formula
α	$(Ca_{1-x}, Gd_{2x/3})(COO)_2 \cdot H_2O$
δ	$(Gd_{1-x}, Ca_{3x/2})_2(COO)_3 \cdot m'H_2O$
G′	$(Gd_{1-x}, Ca_{3x/2})_2(COO)_3 \cdot n'H_2O$

The formulas are listed in Tables 3 and 4.

Because no β form appears in the mixed crystals prepared at elevated temperatures, this form is evidently less stable toward heat than the α form. When the concentration of calcium ion is very high compared with that of gadolinium ion, the precipitated host lattice must be in the most stable form of whewellite. Owing to the very small amount of the guest gadolinium ions absorbed on the surface or entrapped by successive layers of the host lattice, the total amount of hydrated water of the guest lattice will also be small, and as a result, the α form rapidly aggregates.

When the concentration of gadolinium ions exceeds 2%, the number of water molecules brought into the lattice would be much greater than in the former case, and they may be capable of changing the monohydrate into the dihydrate of calcium oxalate. In other words, the host lattice of the whewellite-like phase is smoothly transformed into the other host lattice of weddellite-like phase following the reinforcement of gadolinium ions together with an abundant supply of hydrated water, resulting in the formation of the β form.

At elevated temperatures gadolinium ions are capable of migrating gradually into the lattice of calcium oxalate monohydrate up to a large amount without altering any spacing of the latter; as a result, words, the substitution of calcium ions by gadolinium ions in the α form phase under the experimental conditions can preceed to a great extent, sometimes expanding into the range of the δ form.

On the other hand, the G′ form phase does not admit calcium ions into its lattice to an extent greater than a few percent. It follows that the phase of the δ form may be considered as a distorted phase of the G′ form. With reference to Table 2, it is seen that any one set of spacings, possibly regarded as characteristic of the δ form, is almost identical with that of the G′ form, or with only a very slight shift.

From the present study, it is tentatively suggested that a metastable solid phase like the β form may coexist temporarily with a more unstable phase like the γ form under ordinary experimental conditions. This is clearly seen from the data on the phases when the gadolinium content reaches 30%, as shown in Table 1. The same fact is observed with the α form and δ form which coexist with each other, as shown in Table 2.