

The Dimorphism and the Crystal Habits of Copper-Oxinate Precipitates

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8-Hydroxyquinoline has been used in the quantitative analysis of copper. Copper-oxinate precipitates as greenish yellow needle form (α -form) at the outset and then change into a green plate form (β -form). The relation between this dimorphism and the condition of the precipitation are shown briefly in Table 1 from the results of many electron micrographs.

Table 1. Relation between the dimorphism and the condition of the precipitation.

Temperature (°C)	Conc. of CuSO ₄ (Mole/l)	Shape of precipitate	
		at the outset	after standing
below 40°	10 ⁻³ ~20 ⁻² above 10 ⁻¹	needle plate (tetra.)	plat (tetra.) no change
above 40°	10 ⁻³ ~10 ⁻² above 10 ⁻¹	needle and plate (hex. rhom.) needle and plate (hex. rhom.)	slight change to plate (hex. rhom.) plate (hex. rhom.)

From analytical results, both α - and β -form copper-oxinate precipitates had the same composition, Cu(C₉H₆ON)₂·2H₂O.

X-ray diffraction patterns of precipitates were recorded on a diffractometer, using Ni filter copper radiation ($\lambda=1.54$ Å). It was recognized that the crystal structure differed from each other. Interplanar spacings of β -form copper-oxinate 2 hydrate had good accordance with the values calculated from the lattice constant which Kruch and Dwiggin reported. The precipitates of β -form copper-oxinate 2 hydrate are hexagonal, rhombohedral or tetragonal form, and the hexagonal form has constant plane angles at 116° and 128°. It is suggested that the flat habit surface of hexagonal plate is (100).

The X-ray pattern of α -form copper-oxinate 2 hydrate is different from that of β -form and the number of diffraction peaks is smaller than that of β -form. This fact suggests that the crystal system of unstable α -form copper-oxinate 2 hydrate belongs to the higher symmetric system such as orthorhombic, tetragonal, etc. Now, copper-phthalocyanine precipitate has also dimorphism. The space group of stable β -form copper phthalocyanine is P_{21/a} as in β -form copper-oxinate 2 hydrate. It has been assumed that the α -form copper-phthalocyanine belongs to tetragonal system, by powder X-ray diffraction by Robinson et al. by electron

ABSTRACTS

microdiffraction by Suito and Uyeda. The interplanar spacings of α -form copper-oxinate 2 hydrate calculated from X-ray diffraction patterns accord with the Hull and Daveys diagram for tetragonal system at the position of about 1.6 for c/a value. The interplanar spacings calculated, by assuming the cell constants as $a=b=6.57\text{\AA}$, $c=15.56\text{\AA}$ and $\alpha=\beta=\gamma=90^\circ$, agreed with the above experimental results with accuracy of 1%.

It is concluded that α -form copper-oxinate 2 hydrate, which precipitates from the solution, transforms into stable β -form, in the same way as in the case of copper-phthalocyanine.

On the Leaching of Domestic Chromite Ore in Sulfuric Acid

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To obtain a pure chromic sulfate electrolyte for the production of metallic chromium, the leaching conditions of a domestic ore (48.7% Cr_2O_3 and 12.6% FeO) in sulfuric acid containing small amount of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ were studied.

Sample : The chromite ore from Numaoshi in Hokkaido was crushed by a Engelbach crusher, and sieved by a standard Tyler sieve.

Operation : Crushed ore was digested in 300-ml. porcelain beaker under atmospheric pressure, or in a 2-l lean-lined autoclave under high pressure. A mixed solution of sulfuric acid and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ was used as leaching solution. After leaching the liquor was filtered. The amounts of Fe and Cr in the filtrate and precipitate were analysed.

Items of experiments :

Table 1. Optimum leaching conditions of Numaoshi chromite.

Leaching conditions	Under atmospheric press.	Under high press		
Size of ore (mesh)	-200	-200		
Conc. of H_2SO_4 (%)	70~80	60	40	20
Leaching temp. ($^\circ\text{C}$)	150~170	150	170	190
Pressure (kg/cm^2)	---	3	7	11
Leaching time (hr)	>2	---	>4	---
Weight ratio of H_2SO_4 to ore	6.6	---	3	---
Weight ratio $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0.15~0.20	0.15~0.20		
Extraction of Cr (%)	90	90		