# The Dimorphism and the Crystal Habits of Copper-Oxinate Precipitates

Eiji SUITO and Eiichi SEKIDO

(Suito Laboratory)

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8-Hydrooxyquinoline has been used in the quantitative analysis of copper. Copper-oxinate precipitates as greenish yellow needle form ($\alpha$-form) at the outset and then change into a green plate form ($\beta$-form). The relation between this dimorphism and the condition of the precipitation are shown briafly 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° | $10^{-3}\sim20^{-2}$ | needle | plat (tetra.) |
| | above $10^{-1}$ | plate (tetra.) | no change |
| above 40° | $10^{-3}\sim10^{-2}$ | needle and plate (hex. rhom.) | slight change to plate (hex. rhom.) |
| | above $10^{-1}$ | needle and plate (hex. rhom.) | plate (hex. rhom) |

From analytical results, both $\alpha$- and $\beta$-form copper-oxinate precipitates had the same composition, $Cu(C_9H_6ON)_2\cdot2H_2O$.

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 $\beta$-form copper-oxinate 2 hydrate had good accordance with the values calculated from the lattice constant which Kruch and Dwiggins reported. The precipitates of $\beta$-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 $\alpha$-form copper-oxinate 2 hydrate is different from that of $\beta$-form and the number of diffraction peaks is smaller than that of $\beta$-form. This fact suggests that the crystal system of unstable $\alpha$-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 $\beta$-form copper phthalocyanine is $P_{21/a}$ as in $\beta$-form copper-oxinate 2 hydrate. It has been assumed that the $\alpha$-form copper-phthalocyanine belongs to tetragonal system, by powder X-ray diffraction by Robinson et al. by electron

microdiffraction by Suito and Uyeda. The interplanar spacings of $\alpha$-form copper-oxinate 2 hydrate calculated form 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 interplaner spacings calculated, by assuming the cell constants as $a=b=6.57$Å, $c=15.56$Å and $\alpha=\beta=6=90°$, agreed with the above experimental results with accuracy of 1%.

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

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## On the Leaching of Domestic Chromite Ore in Sulfuric Acid

Kiyokado NISHIHARA, Mitsuo KURACHI and Noboru HIROTA

(Sawamura Laboratory)

*Transaction of the Mining and Metallurgical Alumni Association (Suiyo-Kwaishi)*,

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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 $(NH_4)_2Cr_2O_7$ were studied.

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

Operation : Crushed ore was digested in 300-ml. porcelain beaker under atmospheric presssure, or in a 2-l lean-lined autoclave under high pressure. A mixed solution of sulfuric acid and $(NH_4)_2Cr_2O_7$ 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 Numaushi chromite.

| Leaching conditions | Under atomosheric press. | Under high press | | |
|---|---|---|---|---|
| Size of ore (mesh) | −200 | | −200 | |
| Conc. of $H_2SO_4$ (%) | 70~80 | 60 | 40 | 20 |
| Leaching temp. (°c) | 150~170 | 150 | 170 | 190 |
| Pressure (kg/cm²) | ——— | 3 | 7 | 11 |
| Leaching time (hr) | >2 | —— | >4 | —— |
| Weight ratio of $H_2SO_4$ to ore | 6.6 | —— | 3 | —— |
| Weight ratio $(NH_4)_2Cr_2O_7$ | 0.15~0.20 | | 0.15~0.20 | |
| Extraction of Cr(%) | 90 | | 90 | |