NOTES

Coloration of the Calcined Serpentine with Some Heavy Metal Salt Solutions

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During the course of an investigation of the thermal change of serpentine, it was observed that the serpentine calcined at about its dehydroxylation temperature for 30 min was colored with a saturated solution of mercury(II) chloride. Previously no attention appears to have been paid to this fact. The present work was undertaken to make clear the mechanism of this coloration of the calcined serpentine with some metal salt solutions.

Experimental and Results

Materials. The serpentine used was rock from Kuroishimori (Iwate Prefecture), ground to a powder passable through 200-mesh sieve, with the composition: SiO_2 39.29, Fe_2O_3 7.09, Al_2O_3 2.54, CaO 1.10, MgO 38.02, ignition loss 12.51 (moisture 1.20) per cent. About 5-g portions of the serpentine were calcined at various temperatures (500, 600, 700, 800, 900, and 1000°C) for 10 min. The calcined products themselves colored from slightly brownish to brown as the temperature rose as a result of the formation of magnesioferrite and hematite.[1]

The metal salts (mercury(II) chloride, copper(II) sulfate pentahydrate, and silver nitrate) were obtained commercially; aqueous solutions of them at saturated (at room temperature), 1 N, and 0.1 N concentrations were prepared.

Methods. About 1 g of the calcined serpentine was warmed with each of the metal salt solutions (*ca.* 30 cc) in a water bath at 50 or 100°C for 10—15 min under occasional stirring, and then the mixtures were filtered. The colored residues were thoroughly washed with water, and dried at 105—110°C; then their colorations were observed. The results obtained are illustrated in Table 1.

Table 1. Coloration of serpentine with some heavy metal salt solutions

(1) At 50°C, 10—15 min

	Serp. alone	$HgCl_2$ aq.	$CuSO_4$ aq.	$AgNO_3$ aq.
500°C	gy.	f. br.	f. gr.	d. gy.
600	gy.	f. br.	gr.	bl. gy.
700	br. gy.	d. br.	gr.	bl. gy.
800	f. br.	br.	br. gr.	d. br.
900	br.	br.	br.	br.
1000	br.	br.	br.	br.

(2) At 100°C, 10—15 min

	Serp. alone	$HgCl_2$ aq.	$CuSO_4$ aq.	$AgNO_3$ aq.
500°C	br. gy.	d. br.	gr.	bl. gy.
700	br. gy.	d. br.	gr.	bl. gy.
1000	br.	br.	br.	br.

Abbr.: Serp., Serpentine f., faint
br., brown or brownish
bl., black or blackish
d., dark gr., green gy., grey

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[1] H. Mase, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **60**, 1502 (1957); **62**, 793 (1959).

TABLE 2. X-RAY DIFFRACTION DATA OF THE COLORED SPECIMENS

$HgCl_2$ (Serp.)			$CuSO_4$ (Serp.)			$CuSO_4$ (Dunite)			$CuSO_4$ (MgO)			$AgNO_3$ (Serp.)		
15.2°	w	$*^1$	12.35°	s	$*^2$, $*^3$	12.45°	w	$*^2$, $*^3$	14.0°	s	$*^4$	17.5°	w	F
17.5	w	F	14.0	w	$*^4$	14.0	w	$*^4$	16.7	m	$*^3$	17.9	w	$*^5$
22.65	w	$*^1$	16.7	w	$*^3$	16.7	w	$*^3$	18.15	w	$*^4$	23.0	m	F
23.0	w	F	17.5	m	F	17.5	m	F	23.0	s	F, $*^4$	24.0	w	F
24.8	w	?	23.0	m	F, $*^4$	23.0	m	F, $*^4$	28.1	m	$*^3$, $*^4$	24.8	m	?
25.7	w	F	24.0	w	F	24.8	s	$*^3$	30.8	w	$*^3$	25.75	w	F
27.5	w	$*^1$	24.8	m	$*^3$	25.7	w	F	33.7	s	$*^3$	30.0	w	$*^5$
30.7	m	$*^1$	25.75	w	F	28.0	w	$*^3$, $*^4$	35.9	s	$*^4$	32.3	w	$*^5$
31.6	m	?	30.1	w	F	30.0	w	F	36.75	w	$*^4$	32.6	m	F
32.4	w	F	32.5	s	F	30.8	w	$*^3$	38.0	w	$*^2$, $*^3$	33.5	w	?
33.3	m	$*^1$	35.9	m	F, MF, $*^2$	32.45	m	F	39.9	w	$*^2$	35.9	s	F, MF
34.7	w	$*^1$	36.75	s	F, $*^4$	33.45	w	$*^2$	41.55	w	$*^2$	36.75	s	F
35.85	w	F, MF, $*^1$	38.5	w	?	35.85	m	F, MF, $*^2$	42.5	w	$*^3$	39.0	w	?
36.7	w	F	39.9	w	F, $*^2$	36.75	m	F, $*^4$	43.65	w	$*^4$	39.7	w	F, $*^5$
39.9	w	F	40.3	w	F	38.9	w	?	45.1	w	$*^2$, $*^4$	40.25	w	F
40.2	w	F	42.0	w	F, $*^2$	39.8	w	F, $*^2$	46.5	w	$*^4$	52.35	m	F, $*^5$
41.9	w	F	52.6	s	F, $*^4$	40.25	m	F	48.6	w	$*^2$	56.3	m	F
44.4	w	F	55.1	w	F	42.0	w	F, $*^2$	50.35	w	$*^3$	57.0	w	F
52.5	w	F	56.4	w	F	43.6	w	MF, $*^4$	52.9	m	$*^4$	62.0	w	F
56.25	w	F	57.1	w	F	48.7	w	$*^2$	55.0	w	$*^4$	62.2	w	$*^5$
57.1	w	F, $*^1$	58.9	w	F	52.75	w	F, $*^4$	58.0	w	$*^3$	63.0	w	MF
59.0	w	F	62.1	w	F	57.0	w	F	59.5	w	$*^3$	67.25	w	F
			63.0	w	F, $*^3$	58.25	w	?	60.5	w	$*^4$			
			67.25	w	F	62.2	w	F	63.9	w	$*^4$			
			69.7	w	F	63.0	w	F, $*^3$	66.9	w	$*^4$			

Abbr.: F, Forsterite, MF, Magnesioferrite.

$*^1$ $Hg_4O_3Cl_2$, $*^2$ $Cu_3(SO_4)_2(OH)_2 \cdot 4H_2O$ $*^3$ $Cu_4SO_4(OH)_6 \cdot H_2O$, $*^4$ $Cu_4SO_4(OH)_6$, $*^5$ $Ag_7O_3NO_3$.

Table 1 shows that, when the mixtures were warmed at 50°C, the coloration was difficult to observe, but when the mixtures were warmed at 100°C, the coloration was clearly observed, in the specimens calcined at about 500°C for 10 min; in both cases, the coloration was remarkable in specimens calcined at about 700°C for 10 min. As the heating temperature is raised still more, the coloration becomes weaker; at 1000°C no coloration with the metal salt solutions was observed.

X-Ray Examinations. In order to identify the colored substances, X-ray examinations were carried out for the most intensely colored specimens (heated at 700°C for 10 min). The results obtained are listed in Table 2.

The following compounds were thus identified: basic mercury(II) chloride ($Hg_4O_3Cl_2$), basic copper(II) sulfates (probably a mixture of $Cu_3SO_4(OH)_6 \cdot H_2O$, $Cu_4(SO_4)_2(OH)_2 \cdot 4HO_2$, $Cu_3SO_4(OH)_6$, *etc.*), and basic silver nitrate ($Ag_7O_3NO_3$). Generally speaking, all these colored compounds are basic salts.

Circumstantial Tests. In order to confirm these results, tests for obtaining circumstantial evidence were performed: (1) On dissolving these colored basic salts with nitric acid (for the specimens colored with mercury(II) chloride) or ammonium hydroxide (for the specimens colored with copper(II) sulfate and with silver nitrate), all the specimens were decolorized and showed the color of the calcined serpentine alone. (2) The chloride ions of basic mercury(II) chloride were detected by the precipitation of silver chloride from its nitric acid solution; the sulfate ions of basic copper(II) sulfates were detected by the precipitation of barium sulfate from its ammoniacal solution acidified by hydrochloric acid. However, the nitrate ions of basic silver nitrate could not be certainly detected by either the nitron reaction or the brown-ring test. (3) When strongly heated, the specimens colored with silver nitrate and copper(II) sulfate solutions turned black as a result of formation of metallic silver and copper(II) oxide respectively, while the specimen with a mercury(II) chloride solution turned brownish (the color of the calcined serpentine alone). These changes are shown as the following equations:

$$Ag_7O_3NO_3 = 7Ag + NO_2\uparrow + 2O_2\uparrow$$

$$Cu_{(m+n)}(SO_4)_m(OH)_{2n} \cdot wH_2O = (m+n)CuO + mSO_2\uparrow + m/2\ O_2\uparrow + (w+n)H_2O\uparrow$$

$$Hg_4O_3Cl_2 = 3Hg\uparrow + 3/2\ O_2\uparrow + HgCl_2\uparrow \text{ (sublime)}$$

Discussion

It is generally believed that serpentine forms an amorphous, active phase, probably composed of amorphous forsterite and silica, on its dehydroxylation.[1] Therefore, the coloration of the calcined serpentine seems to be intimately related to the presence of the amorphous, active phase; in other words, either forsterite or silica in this phase plays an important role in the coloration—namely, the formation of the colored basic salts.

For the purpose of making this clear, dunite from the Akaishi Mine (Ehime Prefecture) (SiO_2 37.60, Fe_2O_3 9.16, CaO 0.41, MgO 48.63, ignition loss 3.75 (moisture 0.14) per cent), commercial magnesium oxide, and commercial silica gel were treated with the copper(II) sulfate solution as described above. The results are summarized in Table 3.

TABLE 3. COLORATIONS OF DUNITE, MAGNESIUM OXIDE, AND SILICA GEL WITH COPPER(II) SULFATE SOLUTION
(At 100°C, 10 min)

	Dunite	MgO	Silica gel
180°C	f. gr.	blue	f. blue
750	gr.	blue	f. blue
1000	br.	blue	no color

Abbr.: *Cf.* Table 1.

Of these specimens, dunite alone showed substantially the same coloration as serpentine; therefore, the coloration of the calcined serpentine appears to be primarily the result of the forsterite in the amorphous, active phase. The action of amorphous silica in the phase is uncertain; however, the results for silica gel powder suggest that it is not very great, even if the amorphous silica reacts with the metal salt solutions. Magnesium oxide showed the brightest coloration with the copper(II) sulfate solution, and the X-ray diffraction peaks of its colored specimen were coincident with the majority of those of serpentine and dunite. Furthermore, the difference in color tone between the colored dunite and magnesium oxide appears to be caused by the coexistence of impurities (*e.g.*, iron(III) oxide and magnesioferrite) and to the difference in base strengths. Therefore, it is reasonable to think that the magnesium oxide of the forsterite causes the following reactions with the metal salt solutions:

$$3MgO + 4HgCl_2 = Hg_4O_3Cl_2 + 3MgCl_2$$

$$MgO + 3CuSO_4 + 5H_2O = Cu_3(SO_4)_2(OH)_2 \cdot 4H_2O + MgSO_4$$

$$3MgO + 4CuSO_4 + 3H_2O = Cu_4SO_4(OH)_6 + 3MgSO_4$$

$$3MgO + 4CuSO_4 + 4H_2O = Cu_4SO_4(OH)_6 \cdot H_2O + 3MgSO_4$$

$$3MgO + 7AgNO_3 = Ag_7O_3NO_3 + 3Mg(NO_3)_2$$

The magnesium ions released from the magnesium oxide upon the coloration were detected in the filtrates.

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