

CLXXXIX.—*The Action of Sulphuric Acid on
Nickel-Copper Matte.*

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THE largest source of nickel is the ore found at Sudbury, Ontario, which contains 2—6% of this metal and about the same amount of copper. In order to increase the proportion of nickel in the roasted ore, the matte is leached with 10% sulphuric acid at 80°; two-fifths of the copper is removed as sulphate, but the nickel oxide is so slightly attacked that the residue contains about 50% of nickel (Gowland, "Metallurgy of Non-ferrous Metals," 1921, p. 554).

In view of the positions of nickel and copper in the electrochemical series of elements, and of the fact that copper forms basic salts more readily than nickel, this difference in behaviour is noteworthy. Since we have shown (preceding paper) that nickelous oxide prepared at or above 800° is very inert towards sulphuric

acid, it appeared that the insolubility of the nickel oxide in the matte might be caused by the formation of the inactive variety during the roasting of the ore.

The action of sulphuric acid on mixtures of copper and nickel oxides (prepared under different conditions) has therefore been studied, and the results give information as to the composition of the roasted ore.

EXPERIMENTAL.

The action of *N*/10-sulphuric acid on the following was investigated: (a) A mixture of cupric and nickelic oxides; (b) a mixture of cupric and nickelous oxides prepared at different temperatures; and (c) oxides obtained by heating a mixture of nickel and copper nitrates to various temperatures.

The bivalent oxides were prepared by heating Merck's pure nitrates in an electric furnace, at 800° for copper, and at various temperatures between 400° and 1000° for nickel. Nickelic oxide (from British Drug Houses, Ltd.) was found to be free from impurities. *N*/10-Sulphuric acid was prepared from Merck's pure acid.

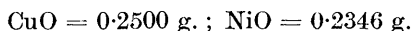
To the mixed oxides in known molecular proportion, sulphuric acid was added in amount insufficient to dissolve them completely. The reaction mixture was kept in a thermostat and stirred continuously. After 7 hours, when no more dissolution of the oxides took place, the solution was filtered, and analysed as follows. It was first acidified and its copper content determined by electrolysis at 2.3 volts; excess of ammonium hydroxide and a small amount of ammonium sulphate were then added, and the nickel was deposited from the solution heated to 70° at 3—4 volts.

(a) *The action of sulphuric acid on a mixture of cupric and nickelic oxides.* Equimolecular proportions of the two oxides were submitted to the action of the acid at 50°; as the following table shows, only a small amount of copper goes into solution when nickel is present as this oxide in the mixture.

$$\text{CuO} = 0.2500 \text{ g.}; \text{Ni}_2\text{O}_3 = 0.4400 \text{ g.}$$

Cu in soln.	Ni in soln.	Ni/Cu in soln.
0.0032 g.	0.1216 g.	38

(b) *The action of sulphuric acid on a mixture of the bivalent oxides.* Equimolecular proportions of copper oxide (prepared at 800°) and of nickelous oxide (prepared at various temperatures) were mixed and the reaction with sulphuric acid was studied at 50°.



Temp. of preparation of NiO	400°	500°	700°	800°	900°	1000°
Cu in soln., g.	0.1438	0.1450	0.1487	0.1548	0.1550	0.1552
Ni in soln., g.	0.0125	0.0072	0.0055	0.0012	0.0010	0.0004
Ni/Cu in soln.	0.0869	0.0496	0.0370	0.0077	0.0064	0.0026

These results indicate that the relative solubility of nickelous oxide is slight and decreases rapidly as the temperature of its preparation is increased.

The effect of temperature on this reaction was next studied. Both oxides prepared at 800° were mixed in equimolecular proportion and the reaction was carried out at various temperatures. It is evident that the amount of nickel dissolving increases about 2½ fold as the temperature of the acid is increased from 50° to 80°.

CuO = 0.2500 g. ; NiO = 0.2346 g.

Temp. of reaction.	Cu in soln., g.	Ni in soln., g.	Ni/Cu in soln.
50°	0.1550	0.0012	0.0077
70	0.1520	0.0020	0.0132
80	0.1489	0.0027	0.0181

The proportion of nickelous oxide in the mixture was then increased, but no change was found in the amount of nickel going into solution at 50°. (Oxides prepared at 800° were used for this purpose.)

CuO, g.	NiO, g.	Molar ratio CuO : NiO.	Cu in soln., g.	Ni in soln., g.
0.2500	0.2346	1 : 1	0.1550	0.0012
0.2500	0.4692	1 : 2	0.1550	0.0012

(c) *The action of sulphuric acid on oxides obtained by heating the mixed nitrates.* The finely powdered nitrates in molecular proportion were heated to various temperatures. The colour of the mixed oxides was reddish-brown, deepening with increasing temperature. Analysis showed the composition of the mixed oxides to differ from the theoretical by 2.5% for the mixture obtained at 400° and by 0.4% for that obtained at 800°.

The amount of nickel dissolving in sulphuric acid at 50° from these mixtures decreased as the temperature of preparation of the mixed oxide was raised :

Mixture taken = 0.4846 g.

Temp. of preparation of the oxide.	Cu in soln., g.	Ni in soln., g.	Ni/Cu in soln.
400°	0.0336	0.0968	2.881
500	0.0924	0.0604	0.654
700	0.1432	0.0160	0.112
800	0.1460	0.0094	0.064

It was observed that the residue had a reddish tinge, brighter than that of the original oxide; hence the residue, from mixed oxides (prepared at 800°) and excess sulphuric acid, was analysed (0.2607 g. gave 0.0552 g. of CuO and 0.2055 g. of NiO; whence CuO : NiO = 1 : 3.968). These results indicate, first, that an excess of sulphuric acid is not able to remove copper oxide completely from the mixed

oxides, and, secondly, that the residue approximates to the composition $\text{CuO}, 4\text{NiO}$.

To test this observation further, copper and nickel nitrates mixed in different ratios were heated to 800° , the oxides obtained were heated with excess of sulphuric acid for 7 hours, and the solutions analysed.

Molar ratio $\text{Cu}(\text{NO}_3)_2 : \text{Ni}(\text{NO}_3)_2$.	Oxide taken, g.	Cu in soln., g.	Ni in soln., g.
1 : 1	0.4846	0.1558	0.0251
1 : 2	0.7192	0.1100	0.0055
1 : 4	1.1884	0.0040	0.0050

These results show that the amount of copper oxide dissolved is small when the ratio of copper to nickel oxides in the mixture is 1 : 4. When a mixture of copper and nickel oxides, prepared separately at 800° , is treated with excess of sulphuric acid, however, all the copper oxide dissolves. These experiments suggest the existence of a compound, $\text{CuO}, 4\text{NiO}$, which does not react appreciably with sulphuric acid.

Discussion of Results.

The foregoing results show that sulphuric acid dissolves nickel far more readily from mixtures of its trioxide with cupric oxide than from similar mixtures of its bivalent oxide. In the latter case, the amount of nickel dissolved decreases as the temperature of preparation of the oxide is raised, increases with increasing temperature of the sulphuric acid, and remains unaffected by change in the ratio of nickelous to cupric oxide. These findings, when compared with the action of sulphuric acid solution on the nickel-copper matte, indicate that during the roasting of the nickel ore nearly all the nickel is converted into the inactive variety of nickelous oxide. A small amount of nickelic oxide may also be formed along with the inactive lower oxide and may be responsible for the fact that 1—2% of nickel goes into solution along with copper sulphate. Further, it is probable that a complex oxide of copper and nickel, like the one obtained by heating the nitrates, is formed during the roasting of the ore. The solubility of this complex oxide in sulphuric acid is very low if it is prepared at or above 800° : its formation would account both for the negligible loss of nickel from the matte on treatment with sulphuric acid and for the incomplete removal of copper.

Langer (*J. Soc. Chem. Ind.*, 1917, **36**, 1135) has found that if the roasted ore after the treatment with sulphuric acid solution be mixed with a solution of copper sulphate, some nickel goes into solution as nickel sulphate; this may be due either to (1) the

action of sulphuric acid on one of the oxides of nickel in the matte or to (2) the action between nickel oxide and aqueous copper sulphate. The amount of nickel going into solution in the second process has been measured and found to be small, yet it contributes to the amount dissolving from the nickel-copper matte.

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