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RECOVERY OF MINERAL VALUES IN CUPRIFEROUS AND NICKELIFEROUS PYRRHOTITE

By Oliver C. Fursman

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
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RECOVERY OF MINERAL VALUES IN CUPRIFEROUS AND NICKELIFEROUS PYRRHOTITE[1]

by

Oliver C. Fursman[2]

SUMMARY

These investigations were conducted to determine conditions for recovery of nickel and copper from Funter Bay, Alaska, sulfide ore and recovery of nickel from nickel-silicate ore, Nickel Mountain, Riddle, Oreg. Samples of Funter Bay cupriferous and nickeliferous pyrrhotite ore, were treated by beneficiation, roasting, electric smelting of roasted ore for matte production, chlorination, leaching, and sulfatizing roasting with subsequent leaching. Funter Bay and Nickel Mountain ores were smelted together to produce matte.

Total sulfide flotation, followed by magnetic separation of the tailings to recover entrained nickel-bearing pyrrhotite, resulted in the highest nickel recovery in beneficiation tests on Funter Bay ore. Overall beneficiation resulted in recovery of 98.5 percent of the copper and 95.4 percent of the nickel in the concentrate that contained 3.5 percent copper and 1.7 percent nickel.

Sulfatizing roasting followed by water leaching was the only treatment that resulted in recoveries of copper and nickel which may have commercial application. Copper recovery approaching 100 percent was achieved by grinding ore samples to 200-mesh size. It was necessary, however, to grind samples to 90 percent passing 325-mesh in order to obtain 72 percent nickel recovery.

Precise control of temperature and duration of roasting of Funter Bay ore was required to obtain maximum recoveries of copper and nickel and minimize iron solubility in the leach solution. Best results were obtained when the roasting was done in three stages, and at the following temperatures: First, 370° to 450° C.; second, 455° to 550° C.; and third, 590° to 600° C. The first stage was completed when the excess sulfide sulfur was burned off and evolution of sulfur dioxide subsided. At the end of stage one, most of the copper, up to one-half of the nickel, and about one-fifth of the iron were sulfatized and water soluble. Completion of the second stage was indicated when sulfur trioxide fumes subsided and the ore lost most of its magnetic properties and turned

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[1] Work on manuscript completed December 1961.

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ferric-oxide red. On completion of stage two, practically all of the copper, more than one-half of the nickel, and about one-tenth of the iron were in water-soluble form. The third stage, during which most of the ferric sulfate decomposed, was terminated when sulfur trioxide evolution practically ceased. Sulfatizing of nickel continued during the third stage and solubility of iron decreased further to about 2 percent. Test results indicated that rabbling during the second- and third-stage roasts was beneficial in obtaining higher recoveries of copper and nickel.

INTRODUCTION

The United States, in 1959, produced only about 10 percent of its nickel requirements. One of the Bureau of Mines programs, of which this investigation is a part, is to develop processes for increasing nickel production from domestic ores. In the Pacific Northwest and Alaska there are known deposits of pyrrhotite that contain appreciable amounts of both nickel and copper. These deposits, however, are widely separated and the reserves are too limited and too low in mineral contents to have attracted exploitation up to the present time. One of the larger known of such deposits of nickel-copper-bearing ores is the Stillwater Complex in Montana. It is estimated[3] that individual pods and lenses in this area contain from 1,000 to over 1 million tons of sulfide-bearing material. During the past several years, investigations were conducted at the Albany Metallurgy Research Center to develop practicable and economic methods for recovering nickel, copper, and other mineral values from these sulfide ores.

Although other avenues of approach were studied and explored, sulfatizing roasting followed by water leaching appears to hold promise as a successful procedure for treating copper-nickel sulfide ores. Ashcroft,[4] [5] working with Rhodesian ores, found that reaction in roasting proceeds primarily and definitely to the formation of copper sulfates and not oxides, and that the formation of oxides and liberation of SO_2 are secondary reactions caused by the decomposition of previously formed sulfates. The samples tested were selected or mixed so that the charge for the roaster contained an equivalent basic carbonate or oxide for every equivalent of sulfur present. Further findings of Mr. Ashcroft are as follows:

1. Iron oxide probably acts as an efficient catalyzer in the formation of copper, zinc, and nickel sulfates.

2. At temperatures above 550° C., or thereabouts, formation of cupric ferrite ($CuO \cdot Fe_2O_3$) begins when copper oxide and iron oxide are brought into

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[3] Roby, Robert N. Investigation of Copper-Nickel Deposits of the Stillwater Complex, Stillwater and Sweetgrass Counties, Mont. BuMines Rept. of Investigations 4431, 1949, 10 pp.

[4] Ashcroft, Edgar A. Sulfate Roasting of Copper Ores and Economic Recovery of Electrolytic Copper From Chloride Solutions. Trans. Am. Electrochem. Soc., v. 63, 1933, pp. 23-50.

[5] Ashcroft, Edgar A. Treating Ores or Concentrates of Copper and Nickel. U.S. Pat. 1,851,885, Mar. 29, 1932.

juxtaposition, and even at 700° C. the reaction is prohibitively rapid. Cupric ferrite is insoluble in any dilute acid-leaching solution normally used in copper leaching.

3. The ordinary rabbled furnace is inimical to the production of all-water-soluble copper sulfate by reason of the omnipresent reaction:

$$CuSO_4 + CuS + O_2 \rightarrow 2CuO + 2SO_2.$$

4. A reaction similar to the above resulting in the decomposition of sulfates is apt to occur in the presence of carbon or of any reducing gas, such as flue gas:

$$CuSO_4 + CO \rightarrow CuO + SO_2 + CO_2.$$

5. Iron sulfate is not, as is usually stated, decomposed at a temperature so far below the decomposition temperature of copper sulfate that a mere roasting at a carefully regulated temperature may be employed to produce, quantitatively, soluble copper and insoluble iron.

Peretti[6] refuted the claim of Ashcroft that copper oxide production resulted only from secondary decomposition of sulfates that were formed as primary products. He showed that a layer of Cu_2O appeared directly adjacent to the Cu_2S during roasting of briquettes of cupric sulfide, CuS. The reactions proposed were:

$$2CuS \rightarrow Cu_2S + 1/2S_2$$

$$1/2S_2 + O_2 \rightarrow SO_2$$

$$Cu_2S + 3/2O_2 \rightarrow Cu_2O + SO_2$$

$$Cu_2O + 1/2O_2 \rightarrow 2CuO.$$

At temperatures above 663° C., CuO was the only final solid phase reported. Below 663° C., increasing amounts of sulfate were found mixed with the CuO. When the outer layer was wholly CuO, it was black, porous, and easy to cut with a knife. The specimens containing sulfate became harder and less porous as the sulfate content increased until at 478° and 430° C., the pieces became so hard and dense as the holding time increased that the reaction practically ceased in a CuO layer between 3 and 4 millimeters in thickness.

Investigation by McCabe and Morgan[7] supports the claim of Peretti. They reported the following sequence of products, beginning at the sulfide surface, when roasting discs of synthetic chalcocite at 600° C.: Cu_2O, a mixture of Cu_2O and $CuSO_4$, $CuSO_4$, $CuO \cdot CuSO_4$, and CuO at the outer surface. The principal reactions were reported to be:

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[6] Peretti, E. A. A New Method for Studying the Mechanism of Roasting Reactions. Discussions Faraday Soc., 1948, vol. 4, p. 174.

[7] McCabe, C. L., and J. A. Morgan. Studies on the Oxide and Sulfate Layers Formed During Roasting of Sulfides. J. Metals, 1956, vol. 8, p. 800A.

$$Cu_2S + 3/2O_2 \rightarrow Cu_2O + SO_2$$

$$Cu_2O + 2SO_2 + 3/2O_2 \rightarrow 2CuSO_4$$

$$2CuSO_4 + \Delta \rightarrow CuO{\cdot}CuSO_4 + SO_3$$

$$CuO{\cdot}CuSO_4 + \Delta \rightarrow 2CuO + SO_3 .$$

They explained the formation of sulfates as follows: SO_2 diffuses out through the pores in the Cu_2O to a position where the oxygen and SO_2 pressures have values fulfilling thermodynamic conditions for the formation of $CuSO_4$. The SO_3 gradient decreases from the sulfate layer toward the oxygen gas phase, causing the $CuSO_4$ to decompose to form the basic sulfate which in turn decomposes into CuO and SO_3.

Thornhill and Pidgeon[8] studied the roasting of sulfides and reported the formation of firm, protective oxide shells when roasting pentlandite particles at temperatures below 650° C. They suggested that much of the oxide growth took place by ionic migration through the continuous oxide layer. The oxidation rate was found to increase with fineness of grind when roasting pyrrhotite. Whereas 65- to 80-mesh particles roasted linearly at 550° C., the oxidation rate of 30- to 40-mesh particles was retarded after the formation of about 160 microns of oxide. The roasted pyrrhotite particles were deeply penetrated by oxide columns. The studies showed that selective oxidation took place when roasting chalcopyrite and pentlandite, resulting in concentration of copper in the former and nickel in the latter, the iron being first to oxidize in particles of each material.

Wadsworth[9] and associates confirmed the results reported by McCabe and Morgan[10] and Thornhill and Pidgeon[11] in the study of the oxidation of chalcocite, Cu_2S. Their study of sulfatizing Cu_2S indicated that, in general, oxidation reactions take place by diffusion. However, entrapped gases in certain temperature ranges almost stop oxidation before the process is completed. The individual steps in roasting at 750° C. were reported as follows:

$$Cu_2S \rightarrow Cu_{1.8}S \rightarrow Cu_2O \rightarrow CuSO_4 \rightarrow CuO{\cdot}CuSO_4 \rightarrow CuO.$$

Cuprous oxide was converted to copper sulfate and other products by heating the oxide in mixtures of SO_2 and O_2 of known ratios and at various temperatures. Based on the accepted solid-state diffusion theory in copper oxidation,[12] the authors explained the oxidation of Cu_2S by the following postulated reactions:

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[8] Thornhill, P. G., and L. M. Pidgeon. A Microscopic Study of Sulfide Roasting. Trans. AIME, v. 209, 1957, pp. 989-995.

[9] Wadsworth, M. C., K. L. Leiter, W. H. Porter, and J. R. Lewis. Sulfating of Cuprous Sulfide and Cuprous Oxide. Trans. AIME, v. 218, June 1960, pp. 519-525.

[10] Work cited in footnote 7.

[11] Work cited in footnote 8.

[12] Bardeen, J., W. H. Brattain, and W. Shockley. Investigation of Oxidation of Copper by Use of Radioactive Cu Tracer. J. Chem. Phys., 1946, v. 14, p. 714.

$$Cu_2S \rightarrow Cu_{1.8}S \text{ (digenite)} + 0.2Cu^+ \text{ (ion)} + 0.2e \text{ (electron)}$$

$$Cu^+ + e \rightarrow \text{diffusion through digenite}$$

$$Cu_{1.8}S + 1.45O_2 \rightarrow 0.9Cu_2O + SO_2.$$

The anomolous effect of SO_2 in accelerating the oxidation of Cu_2O to CuO at 850° C. was explained by the theory that SO_2, or probably SO_3, produces a potential at the CuO surface, thereby increasing the rate of diffusion of Cu^+ through CuO, which probably adds complexity to lower temperature reactions where sulfates are stable.

Lewis[13] and associates determined that optimum temperature for oxidation of chalcocite to give water-soluble copper is about 450° C., with both air and oxygen, and oxygen is a more effective oxidizing agent than air for conversion to water-soluble substances. At about 450° C. the following reactions were confirmed:

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

$$2CuO + Cu_2S \rightarrow 4Cu + SO_2.$$

The authors also determined that basic copper sulfate begins to form at a little above 300° C. and in the presence of cupric oxide the temperature of formation is probably much lower because of the reaction:

$$CuO + CuSO_4 \rightarrow CuO \cdot CuSO_4.$$

Charles T. Baroch[14] working with copper ore at Bagdad, Ariz., reported that roasting a concentrate for hydrometallurgical purposes is more complicated than ordinary oxidation roasting to remove sulfur. His observations indicated that reactions take place in three distinct stages, which may overlap to some extent, but which take place only in the order given. Also, each stage requires a definite temperature range and the best oxidation conditions possible in order to be completed within practical time limits. Using the following sulfatizing roasting conditions, he was successful in almost completely transforming the copper into a water-soluble state:

1. First stage: 370° to 380° C. during which all but traces of true sulfides were decomposed, the sulfur being driven off or oxidized to form sulfates. Temperatures above 455° C. should be avoided before this stage is completed, otherwise a true magnetite will be formed that is difficult to reoxidize to the less soluble ferric form. The probable reaction is:

$$FeS + 10Fe_2O_3 \rightarrow 7Fe_3O_4 + SO_2.$$

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[13] Lewis, J. R., J. H. Hamilton, J. C. Nixon, and C. L. Graverson. Oxidation of Chalcocite in Air Compared With Its Oxidation in Pure Oxygen. Metals Technol., Tech. Pub. No. 2388, June 1948.

[14] Baroch, Charles T. Hydrometallurgy of Copper at the Bagdad Property. Trans. Am. Electrochem. Soc., v. 57, 1930, pp. 205-229.

2. Second stage: 455° to 540° C. is the oxidizing or demagnetizing period, during which the desired higher oxides of copper and iron are formed.

3. Third stage: 590° C. in which the water-soluble sulfates of iron are selectively destroyed.

Klyachko-Gorvich, Bulgakova, and Gerasimov[15] were able to convert pure cobalt oxide or nickelous oxide completely to sulfate at 600° C. by repeatedly pulverizing the compounds in the presence of mixtures of SO_2 and O_2.

The fluid-bed reactor has been proposed for sulfatizing roasting of sulfide ores,[16] using a gas composition of about 8 percent sulfur dioxide and 4 percent oxygen, and installations[17] [18] of this type have been made in various locations.

ACKNOWLEDGMENTS

Special acknowledgment is due the late Dr. John P. Walsted who performed many of the experimental tests included in this report, and W. S. Pekovich, manager of Admiralty-Alaska Gold Mining Co., who furnished the sulfide ore samples used in this investigation.

SAMPLES TESTED

Copper-bearing nickeliferous pyrrhotite ore was obtained from a deposit at Funter Bay, Admiralty Island, Alaska. This material, considered to be similar in chemical composition to other ores found in the Pacific Northwest and Alaska, was received at the Albany Metallurgy Research Center in two different shipments, designated as lots 1 and 2. The samples, which were taken at or near massive sections of the deposit, contained only about 15 percent gangue and were found to be higher in copper and nickel content than the average of the deposit.

A nonsulfide, nickel-bearing ore from Nickel Mountain, Riddle, Oreg., was incorporated in some smelting tests with Funter Bay ore. Analyses of ore samples are shown in table 1.

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[15] Klyachko-Gorvich, L. L., T. I. Bulgakova, and Y. I. Gerasimov. Interaction of Cobalt Oxides With Sulfur Oxides. Zhur. Obschei Khim., v. 18, 1948, pp. 1580-1589; Chem. Abs., vol. 43, 1949, p. 6,931g.

[16] Stephens, Frank M., Jr. The Fluidized-Bed Sulfate Roasting of Nonferrous Metals: Chem. Eng. Prog., v. 49, No. 9, Sept. 1953, pp. 455-458.

[17] Thompson, R. B. and I. G. Roesner. Fluid-Bed Roasting Principles and Practice. Paper pres. AIME, New York, N.Y., Feb. 15, 1960, 26 pp.

[18] Grothe, J. D. and B. H. McLeod. Influence of Fluidized Roasting on Hydrometallurgical Processes. Trans. Internat. Miner. Dressing Cong. 1957 (Stockholm), pp. 675-682 (Pub. 1958).

TABLE 1. - Analyses of samples received, percent

	Cu	Ni	Fe	S	SiO_2	Al_2O_3	CaO	MgO	TiO_2
Funter Bay ore:									
Lot 1.................	3.12	1.84	54.5	32.8	2.0	0.7	1.3	0.9	0.5
Lot 2.................	3.3	1.65	50.1	28.9	-	-	-	-	-
Nickel Mountain ore.....	-	1.2	10.7	.01	54.0	.7	.5	-	-

Petrographic examination of Funter Bay ore indicated that it consists essentially of pyrrhotite, some chalcopyrite, relatively small amounts of magnetite and pyrite, and small amounts of pentlandite, calcite, and serpentine. A detailed polished-surface study revealed that the pentlandite is fine grained, ranging in size from 22 to 88 microns, and is intimately associated with the pyrrhotite. No discrete cobalt minerals were observed. Similar examination of a minus 200-mesh sample that had been given a sulfatizing roast at about 600° C. showed the following composition: (Percentage figures, where given, are based on visual inspection under the petrographic microscope) Iron oxide, 60; amphibole, 10 to 15; partly altered pyrrhotite, 10; pyrite, 10; chalcopyrite, 5 to 10; small amount of chromium spinel, quartz, feldspar, chlorite, rutile; and a trace of zircon. Spectroscopic examination of selected concentrates of this roasted material showed that nickel is intimately associated with the iron oxide and the unaltered pyrrhotite. It was further determined that a small part of the iron oxide occurs in the form of magnetite and that pentlandite, calcite, and serpentine were present.

BENEFICIATION

Beneficiation tests on Funter Bay ore were made to effect concentration of copper and nickel minerals in both roasted and unroasted samples of varying fineness of grinds. Magnetic separation tests on ores and tailings from flotation of copper values failed to produce concentrates in which satisfactory recoveries of both copper and nickel were obtained. More acceptable recoveries of both copper and nickel, however, were achieved by total sulfide flotation followed by magnetic separation of the tailings to recover entrained nickel-bearing pyrrhotite. Copper recovery alone at satisfactory levels was reached by flotation of chalcopyrite, but much of the nickel is contained in pentlandite, which is closely associated with pyrrhotite, and therefore, complete recovery of the pyrrhotite is required to prevent loss of nickel.

Magnetic separation tests were made on both raw ore and ore that had been roasted to 8.9 percent sulfur content. Results of tests on roasted material indicated unsatisfactory separation of the copper, nickel, or iron minerals in ore ground to minus 150-mesh. Magnetic separation of unroasted ore demonstrated that 74 percent of the nickel and 85 percent of the iron could be recovered in a magnetic product containing 1.7 percent nickel and 55.8 percent iron. The nonmagnetic fraction contained 11.9 percent copper and 2.6 percent nickel at recoveries of 87 and 26 percent, respectively.

Beneficiation tests were made on minus 200-mesh roasted and unroasted sulfide ore from which the copper minerals were first removed by flotation. The flotation tailings were then treated by low-intensity wet-magnetic separation, with the rougher magnetic concentrate recleaned once. Best recoveries obtained in the combined flotation and magnetic concentrates were 87 percent copper and 76 percent nickel for the unroasted ore and 94 percent copper and 79 percent nickel for the roasted material.

Magnetic separation tests were conducted, prior to flotation, on samples of roasted and unroasted sulfide ores ground to minus 200-mesh. In each test the magnetic fractions were cleaned twice and the nonmagnetic fractions were combined for flotation. Best recoveries obtained in the combined flotation and magnetic concentrates were 98.3 percent copper and 93.1 percent nickel for the unroasted ore and 82.0 percent copper and 81.9 percent nickel for roasted sample.

An attempt was made to recover copper and nickel values separately from unroasted ore. Copper minerals were separated by flotation of minus 200-mesh material. The tailings were roasted at 750° C. for 2 hours in a muffle furnace and rabbled every 30 minutes. After cooling, the roasted tailings were ground to minus 325-mesh, deslimed, and split into two fractions. One fraction was treated by flotation to remove copper and nickel sulfides while depressing the iron and gangue. The other portion was treated first by low-intensity wet-magnetic separation, after which the nonmagnetic product was treated by flotation to scavenge the remaining copper and nickel. Copper concentrate from the raw material contained 84 percent of the copper at a grade of 23.1 percent; flotation of one portion of the roasting tailing recovered only a small amount of the copper and iron. The copper concentrate from the raw material contained 22.5 percent of the nickel at a grade of 3.12; little concentration of nickel occurred in either the magnetic or flotation concentrates. Magnetic separation of the second portion of roasted tailing material failed to effect material concentration of copper and nickel values in any product.

Laboratory tests were conducted on minus 200-mesh ore to determine conditions for producing total-sulfide concentrate, using xanthates as collectors, a frother, and various regulators for pH control. When sulfuric acid was used to maintain pH of 6.1 to 6.2, best recoveries were 93.4 percent of the copper, 81.5 percent of the nickel, and 66.1 percent of the iron at a grade of 4.26 percent copper, 1.91 percent nickel, and 58.4 percent iron. Flotation tests in an alkaline circuit at a pH of 9.2, using lime and soda ash as regulators, gave recoveries of 97.5 percent of the copper and 93.9 percent of the nickel at a grade of 3.34 and 1.63, respectively. The results of a test using sodium silicate to maintain pH of 9.2 are shown in table 2.

A total-sulfide flotation test on larger scale, followed by magnetic separation to recover the small amount of pyrrhotite entrained in the tailing, resulted in recovery of 98.5 percent of the copper and 95.4 percent of the nickel.

TABLE 2. - Concentration of copper and nickel minerals by laboratory-scale flotation

Product	Weight-percent	Analyses, percent			Recovery, percent		
		Copper	Nickel	Iron	Copper	Nickel	Iron
Concentrate............	61.12	3.66	1.68	50.7	96.85	97.03	86.37
Cleaner tailing........	7.38	.43	.34	14.2	1.38	2.37	2.92
Rougher tailing........	31.50	.13	.02	12.2	1.77	.60	10.71
Calculated head......	100.00	2.31	1.06	35.9	100.00	100.00	100.00

SULFATIZING-ROASTING AND LEACHING

Equipment and Procedure

Ground samples of lot 2 Funter Bay ore were placed in a fire-clay or silica dish and heated in an electric laboratory furnace equipped with automatic temperature control. A thermocouple was placed in the sample to determine its temperature during roasting. Samples that had been ground to minus 10-mesh, minus 200-mesh, and 90 percent minus 325-mesh were tested. Usually, the samples were roasted in three distinct and successive stages or temperature ranges as follows: Stage 1, 370°-450° C.; stage 2, 455°-550° C.; stage 3, 590°-600° C. The effect of initial roasting at temperatures below 370° C. were investigated, and also some samples were given a fourth-stage roast at 700° C. Rabbling, which usually was done in the second and third stages and sometimes in the first stage was performed by hand. Final samples, and samples taken at various stages of roasting, were leached by agitating for 1 hour in water or dilute sulfuric acid solution to determine recovery of copper, nickel, and iron in soluble form.

Roasting Reactions

Based on the chemical properties of the sulfides contained in the samples tested, it is expected that the following reactions will occur on heating Funter Bay ore samples:

$$\text{Pyrite: } FeS_2 + \Delta \rightarrow FeS + S \qquad (1)$$

$$\text{Chalcopyrite: } 2CuFeS_2 + \Delta \rightarrow Cu_2S + 2FeS + S \qquad (2)$$

$$\text{Pyrrhotite: } Fe_7S_8 + \Delta \rightarrow 7FeS + S. \qquad (3)$$

No evolution of elemental sulfur can be expected from heating pentlandite, but the following reaction is possible in the presence of oxygen:

$$FeNiS + 2O_2 \rightarrow FeO + NiO + SO_2. \qquad (4)$$

Other possible reactions in the presence of oxygen:

$$S + O_2 \rightarrow SO_2 \text{ (evolution of } SO_2 \text{ begins at about 260° C.)} \qquad (5)$$

$$SO_2 + 1/2O_2 \rightarrow SO_3 \text{ (}Fe_2O_3\text{ and }SiO_2\text{ catalysts)} \qquad (6)$$

$$NiO + SO_2 + 1/2O_2 \rightarrow NiSO_4 \qquad (7)$$

$$FeO + SO_2 + 1/2O_2 \rightarrow FeSO_4 \qquad (8)$$

$$2FeSO_4 + SO_3 + 1/2O_2 \rightarrow Fe_2(SO_4)_3 \qquad (9)$$

$$Cu_2S + 3/2O_2 \rightarrow Cu_2O + SO_2 \qquad (10)$$

$$Cu_2O + 1/2O_2 \rightarrow 2CuO \qquad (11)$$

$$Cu_2O + 2SO_2 + 3/2O_2 \rightarrow 2CuSO_4 \qquad (12)$$

$$2CuO + Cu_2S \rightarrow 4Cu + SO_2 \qquad (13)$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \qquad (14)$$

$$CuO + SO_3 \rightarrow CuSO_4 \qquad (15)$$

$$2CuO + SO_2 \rightarrow Cu_2O + SO_3 \qquad (16)$$

$$CuSO_4 + CuS + O_2 \rightarrow 2CuO + 2SO_2 \text{ (at about 400° C.)} \qquad (17)$$

$$Fe_2(SO_4)_3 + \Delta \rightarrow Fe_2O_3 \cdot 2SO_3 + SO_3 \text{ (begins at 170° C.)} \qquad (18)$$

$$FeS + 10Fe_2O_3 \rightarrow 7Fe_3O_4 + SO_2 \text{ (about 455° C.)} \qquad (19)$$

$$Fe_2O_3 \cdot 2SO_3 + \Delta \rightarrow Fe_2O_3 + 2SO_3 \text{ (500°-560° C.)} \qquad (20)$$

$$Fe_2O_3 + CuO \rightarrow CuO \cdot Fe_2O_3 \text{ (above 550° C.)} \qquad (21)$$

$$2CuSO_4 + \Delta \rightarrow CuO \cdot CuSO_4 + SO_3 \qquad (22)$$

$$CuSO_4 + CuO \rightarrow CuO \cdot CuSO_4 \qquad (23)$$

$$CuO \cdot CuSO_4 + \Delta \rightarrow 2CuO + SO_3 \qquad (24)$$

$$NiSO_4 + \Delta \rightarrow NiO + SO_3 \text{ (begins at 700° C.).} \qquad (25)$$

Test Results

Test conditions and results are included in table 3 and graphs showing the relationship of metal recoveries and sulfur values to time and temperature of roasts for the most significant tests (10, 11, and 12) are shown in figures 1, 2, and 3.

TABLE 3. - Sulfatizing-roasting and leaching tests

Test	Charge		First stage of roast			Second stage of roast		Third stage of roast		Leach			
	Weight, grams	Mesh size	Duration, hours	Rabble	Temper-ature, ° C.	Duration, hours	Temper-ature, ° C.	Duration, hours	Temper-ature, ° C.	Leach agent	Recovery, percent		
											Cu	Ni	Fe
1...	-	-200	5.5	No	372-400	2.5	538-550	-	-	Hot water[1]	95.4	59.2	13.1
2...	200	-200	4.5	No	370-380	2.5	540-550	1.0	590-600	Cold water	99.7	63.9	6.8
3...	200	-200	6.5	No	370-380	1.5	535-545	1.8	590-600	do.	73.0	44.8	4.0
4...	200	-200	2.0	Yes	350-400	1.0	525-545	5.0	590-600	do.	95.8	65.8	1.9
5...	200	-200	3.5	No	370-380	1.0	530-535	4.2	590-600	do.	79.6	58.8	2.7
6...	200	-10	3.5	Yes	370-425	10.0	450-540	5.0	590-600	do.	89.2	42.4	7.5
7...	200	-10	2.7	No	370-380	3.5	545-560	4.5	590-600	do.	73.1	27.1	2.1
8...	200	-200	2.0	Yes	380-440	1.5	450-530	1.0	580-620	Hot H_2SO_4[2]	98.2	52.4	11.2
9[3] [4]	600	-200	2.0	Yes	390-450	2.5	500-550	1.0	630	do.[2]	87.7	59.4	10.2
9...	600	-200	2.0	Yes	390-450	2.5	500-550	1.0	630	Hot water[1]	-	52.8	2.8
10..	400	-200	7.0	No	380-420	2.0	520	3.0	600	do.[1]	96.8	66.2	3.0
11[5].	400	-200	8.5	No	400	2.0	500	2.0	600	do.[1]	100.0	54.4	2.0
12..	400	(6)	8.0	No	370-450	3.0	500-550	3.0	600	do.[1]	97.2	72.1	3.9
13[7].	400	(6)	8.0	No	375-450	4.0	500-550	3.0	600	do.[1]	58.4	27.8	3.2

[1] Temperature, 90° C.

[2] 25 grams per liter.

[3] Sample given fourth-stage roast for 2 hours at 700° C.; showed following recoveries in acid leach: Cu, 79.8; Ni, 50.6; Fe, 1.2 percent.

[4] Part of the sulfatized residue from test 9 was leached with hot water and part with hot H_2SO_4.

[5] Sample given fourth-stage roast for 1 hour at 700° C.; showed following recoveries in hot-water leach: Cu, 81.4; Ni, 63.0; Fe, 0.2 percent.

[6] 90 percent minus-325.

[7] Ore container covered at end of first-stage roast; no rabbling during second and third stages.

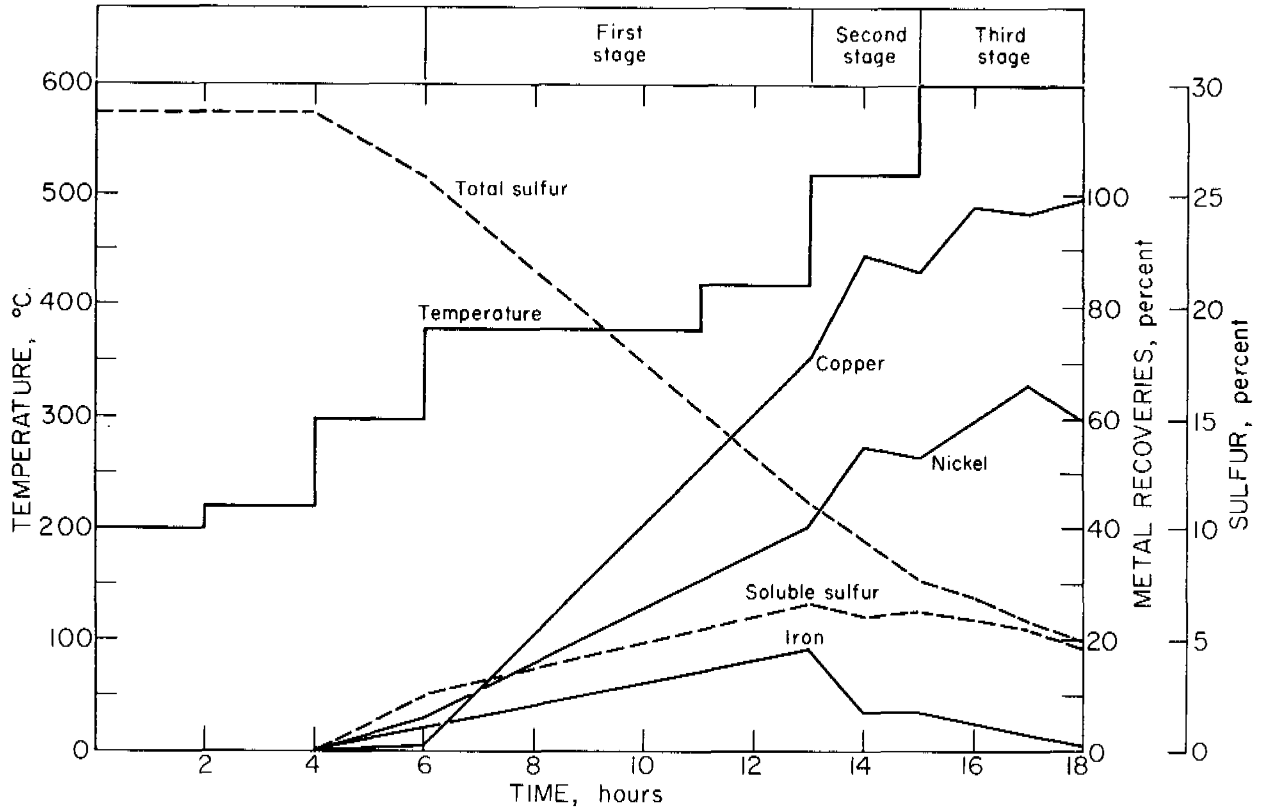

FIGURE 1. - Relationship of Metal Recoveries and Sulfur Values to Time and Temperature of Roast, Test 10.

The recovery of nickel was consistently less than that of copper, which was recovered in amounts up to 100 percent. The highest recovery of nickel (72.1 percent) was obtained in test 12 when roasting and leaching a sample that had been ground to 90 percent passing 325-mesh screen. The material was not rabbled during the first stage at 370°-450° C., but was rabbled during the second and third stages, the temperatures of which were 500°-550° C. and 600° C., respectively. Copper recovery was 97.2 percent and iron recovery 3.9 percent.

Results indicate that fineness of grind affects the recovery of both nickel and copper. The highest nickel recovery was attained when treating the most finely ground ore (90 percent passing 325-mesh). Nickel recovery from minus 200-mesh ore was materially lower at 66.2 percent, and from minus 10-mesh ore, maximum nickel recovery was only 42.4 percent. Copper recovery was not improved by grinding finer than 200-mesh; however, recovery dropped from approximately 100 percent with minus 200-mesh material to 89.2 percent, maximum, when treating minus 10-mesh ore. The fact that nickel occurs in the form of pentlandite, which is finely dispersed and intimately associated with pyrrhotite, may explain in part the reason for lower recoveries of nickel than copper. Also, chalcopyrite, the copper-bearing portion of the ore, decomposes on heating, which breaks up the solid particles and allows oxidizing gases increased contact with the copper sulfide. On the other hand,

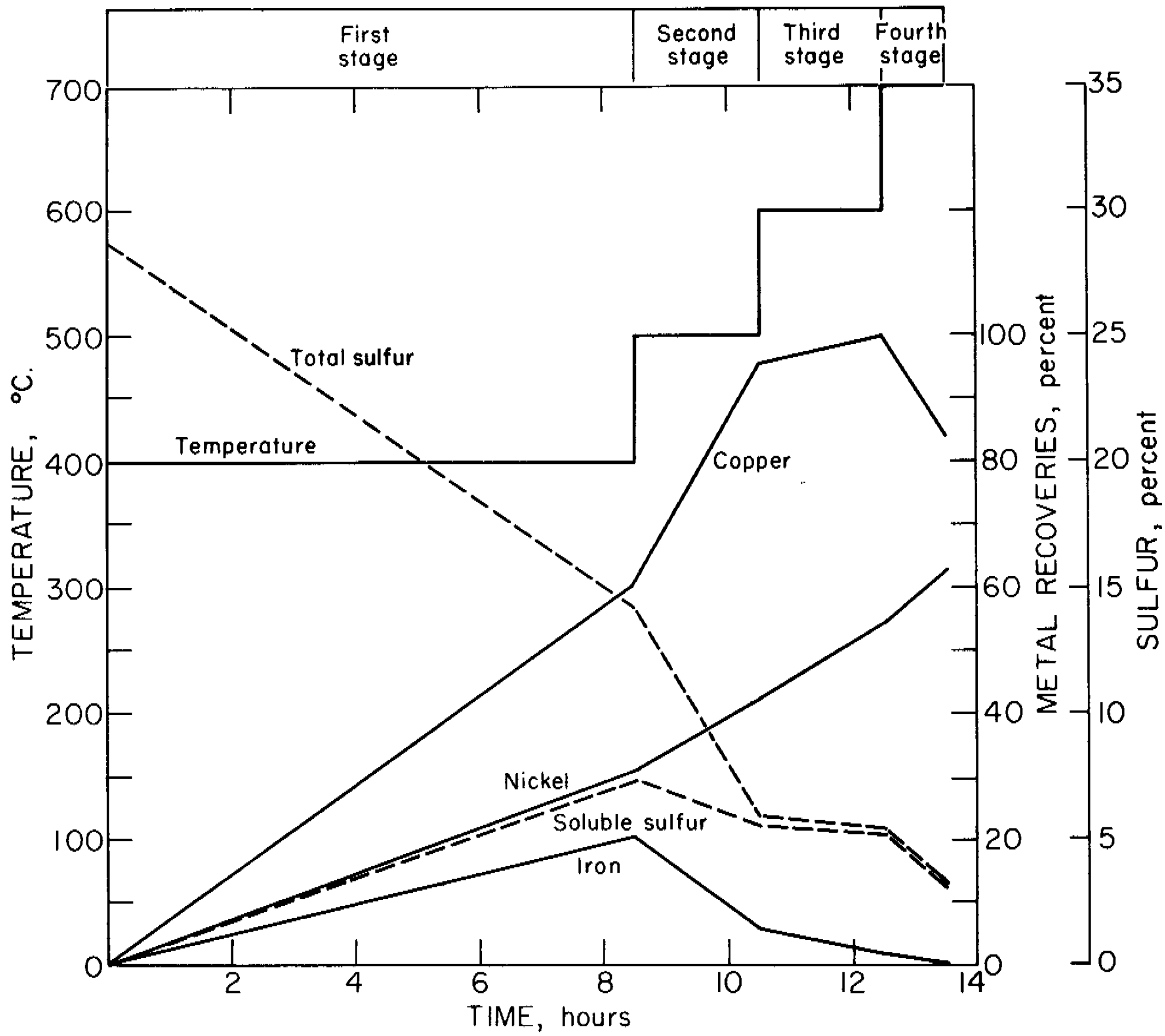

FIGURE 2. - Relationship of Metal Recoveries and Sulfur Values to Time and Temperature of Roast, Test 11.

pyrrhotite, which contains the nickel-bearing pentlandite, does not disintegrate with the expulsion of elemental sulfur during roasting,[19] which limits the contact of oxidizing gases to the nickel sulfide that is exposed on the surface of pyrrhotite particles.

Water was used for leaching in most tests because the solubility of copper, nickel, and iron values in water reflected the actual degree of sulfatization existant at termination of various stages of roasting. The acid leachings recovered some copper, nickel, and iron values in addition to the water-soluble sulfates. Part of the sulfatized residue from test 9 was

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[19] Newton, J., and C. L. Wilson. Metallurgy of Copper. John Wiley & Sons, New York, N.Y., 1942, pp. 65-66.

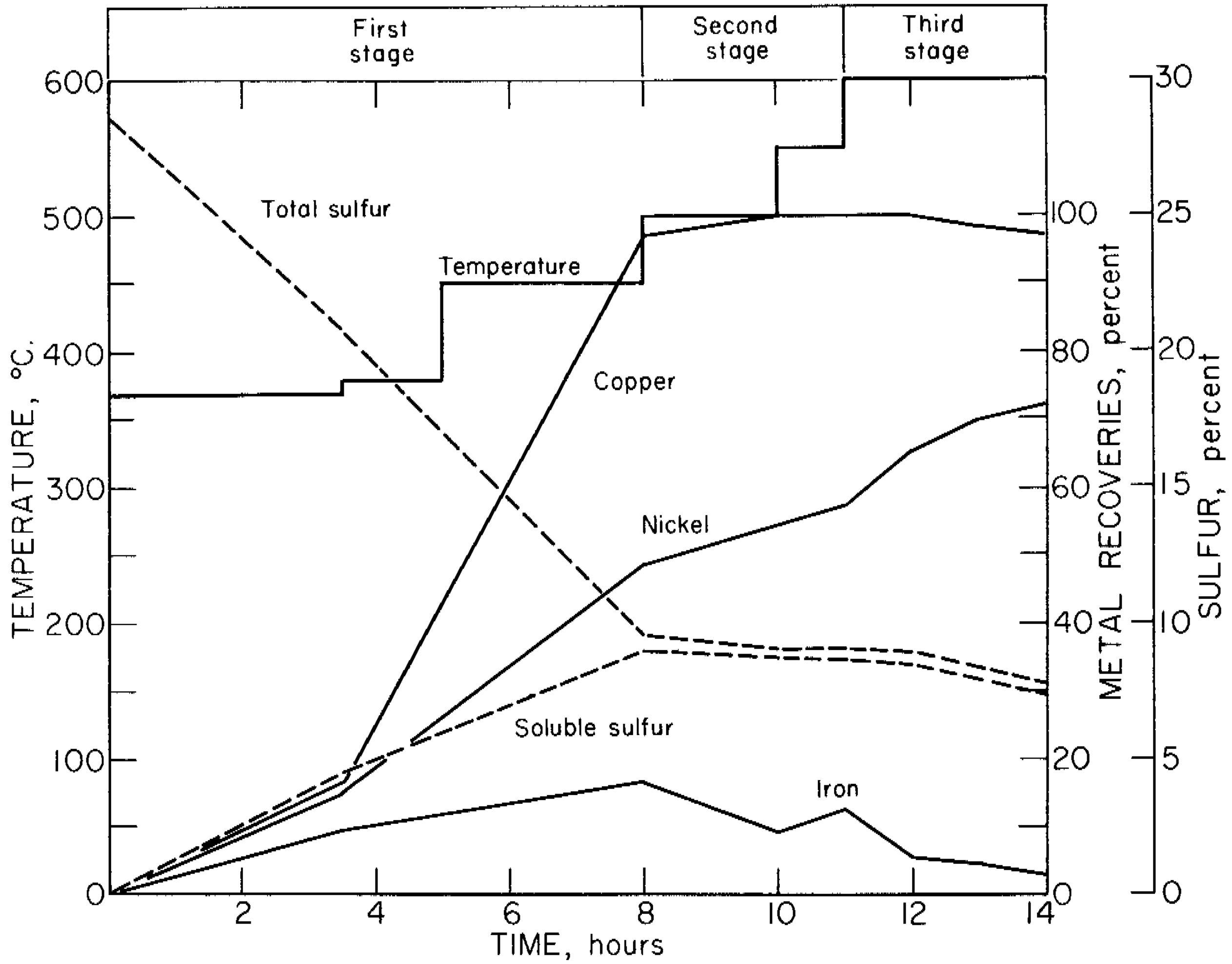

FIGURE 3. - Relationship of Metal Recoveries and Sulfur Values to Time and Temperature of Roast, Test 12.

leached with hot water, and another part was leached with hot dilute sulfuric acid. Nickel recovery from the acid leach exceeded that from the water leach (59.4 and 52.8 percent, respectively); iron recovery, also, was higher in the acid leach, 10.2 percent of the iron being recovered in the acid leach and only 2.8 percent in the water leach. Iron, which is an undesirable component of the leach solution, interferes with final recovery of copper and nickel values.

Based on these laboratory tests, no conclusions of significance can be drawn concerning the time required to complete the various stages of roasting. Thickness of ore bed, rate of rabbling, temperature, and atmospheric conditions affect the time necessary to complete reactions in each stage. Best yields of nickel and copper were obtained in tests during which the sample was not rabbled during the first stage of roasting; however, in these tests up to 8 hours of heating in the temperature range of 370°-450° C. were required before the exit gas showed little or no sulfur dioxide content.

Under the conditions prevailing in the second stage of the roasts, 3 to 4 hours appeared to be adequate to complete the reactions which occur in this temperature range. Only a small amount of ferric sulfate was not decomposed after 2 to 3 hours of heating in the third stage of the roasts.

The recovery and use of possible byproducts would enhance the feasibility of this process. The sulfur dioxide could be recovered and used in sulfite paper pulp manufacture or it could be converted to sulfuric acid which might find a market in some areas. The leach residue, which contained 55 to 60 percent iron, could be raw material in the manufacture of sponge iron, part of which might be useful for precipitation of cement copper from the process leach solutions.

First Stage of Roasts

The objectives of the first stage of each roast were to drive off excess sulfur and convert the copper and nickel compounds, insofar as possible, to sulfates. These objectives were most fully accomplished in test 12 in which sulfur in the residue was mostly in soluble form. Total sulfur content of the sample at the end of the first stage was only 0.7 percent higher than soluble sulfur (fig. 3); the insoluble sulfur present was probably in the sulfide form. At the end of this stage, 97 percent of the copper and 49 percent of the nickel were water soluble. In tests 10 and 11 there was a marked difference between total sulfur and soluble sulfur at the end of stage one, indicating that a considerable quantity of undecomposed sulfides was present. As shown in table 4, the final first-stage roasting temperature of test 12 was 450° C., whereas in tests 10 and 11 the corresponding temperatures were 420° and 400° C., respectively. From this test condition it appears that the temperature during first-stage roasting must be raised to about 450° C. to burn off practically all of the sulfide sulfur.

The results shown in table 4 indicate that final recoveries of copper by water leaching, which were 97 percent or higher at the end of stage three roasts, were not adversely affected by the variations in first-stage roast conditions. Final recoveries of nickel, however, were affected by first-stage roast conditions. Low nickel recoveries at the end of the first stage caused about the same proportionately low recoveries at the end of the third stage.

The insoluble sulfur present at the end of the first-stage roast, test 12, probably was mostly in the pyrrhotite and pentlandite, which do not disintegrate when roasted. The fact that both pyrite and chalcopyrite do disintegrate on heating, together with the high recovery of copper in soluble form supports this probability. Also, if all the insoluble nickel were present as sulfide, it would account for slightly over half of the insoluble sulfur. Because of its small particle size and its intimate association with pyrrhotite, the insoluble nickel was probably present mostly as sulfide, although an appreciable amount could have been in the form of oxide embedded in the surface of pyrrhotite particles. At the end of the first stage, test 12, more than half (51 percent) of the nickel remained insoluble and would have to be sulfatized during the subsequent roasting stages to effect complete recovery.

TABLE 4. - Sulfur values, stage 1 of roast, and metal values, stages 1, 2, and 3 of roasts

	Test		
	11	10	12
Maximum temperature, °C	400	420	450
End of first stage:			
Sulfur, percent:			
Total	14.0	11.3	9.7
Soluble	7.4	6.7	9.0
Difference	6.6	4.6	.7
Recovery, percent:			
Copper	61	71	97
Nickel	32	41	49
End of second stage:			
Recovery, percent:			
Copper	96	87	100
Nickel	43	53	57
End of third stage:			
Recovery, percent:			
Copper	100	97	97
Nickel	55	66	72

The effect of roasting at temperatures below 370° C. in stage one was studied in test 10. The 400-gram sample was first heated at 200° C. for 2 hours, during which time it gained 1.6 grams in weight, although no sulfur dioxide was evolved. Then the sample was heated for 2 hours at 220° C.; no sulfur dioxide was evolved and the sample gained 0.7 grams in weight. Temperature of the sample was gradually raised until sulfur dioxide fumes were detected at 280° C. Heat supply to the furnace was turned off, but heat from combustion of sulfides, even with the door of the furnace closed, raised the ore temperature to 300° C. After 2 hours at this temperature, evolution of sulfur dioxide subsided and the temperature dropped. Sulfatizing of copper and nickel that took place was insignificant, as indicated by the recovery curves of figure 1. On further heating, sulfur dioxide evolution was resumed slightly above 300° C. and the temperature of the sample was allowed to rise from autogenous action. The temperature was held at about 380° C. for 5 hours and then at 420° C. for 2 hours at which time evolution of sulfur dioxide subsided. Analysis of the sample at the end of this period indicated that considerable sulfatization had taken place; the percent solubility of copper and nickel was found to be 71.5 and 41.0, respectively. From this result it may be concluded that 380° C. is near the minimum temperature at which sulfatizing of copper and nickel sulfides may be effected at reasonable rates.

Included among reactions which may occur during the first stage of the roast, equations (1) through (18), are some that are unfavorable for the formation of soluble sulfates of copper. Equation (17) shows the reaction between $CuSO_4$ and CuS in the presence of oxygen in which these two solid compounds are changed to water-insoluble copper oxide. It has been stated[20]

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[20] Work cited in footnote 4.

that this reaction progresses rapidly at about 400° C., and because stirring increases probability of solid contact and reaction between CuS and $CuSO_4$, the ore should not be rabbled during the first stage of the roast. Therefore, most of the tests conducted in this investigation were not rabbled until the end of stage 1, which was indicated by the almost complete subsidence of sulfur dioxide fumes. Owing to the difficulty of holding the temperature within the first-stage range when rabbling during the first stage of the tests conducted, no firm conclusions could be made regarding the advantage or disadvantage of first-stage rabbling. Other unfavorable solid-state reactions that may occur during the first roasting stage and that would be accelerated by rabbling are shown in equations (13) and (14). The claim has been made[21] that first-stage roasting temperatures should not exceed 455° C. to avoid formation, equation (19), of magnetite, which is difficult to reoxidize to the less soluble ferric form.

Based on the foregoing claims, the temperature during stage one of the roasts should be held below 400° C. until most of the sulfide sulfur is burned off and then raised to about 450° C. to fully complete this reaction in reasonable time, being careful to hold the temperature below 455° C. until the sulfide sulfur is completely burned off. Increasing the temperature into the second-stage range before the evolution of sulfur dioxide has subsided will inhibit the objective of oxidizing the metal oxides to the highest state, as indicated by the following typical undesired reaction from equation (16):

$$2CuO + SO_2 \rightarrow Cu_2O + SO_3.$$

Second Stage of Roasts

During the second stage of roasting, continued sulfatization of copper and nickel and oxidation of lower iron oxides were observed. The second-stage period was characterized by evolution of sulfur trioxide, formed by the decomposition of iron sulfates. This gas made possible the sulfatization of oxides of the copper and nickel present. This latter reaction probably also occurred to some extent during the first stage, the sulfur trioxide being generated by oxidation of sulfur dioxide, catalyzed by ferric oxide and silica, equation (6). Almost no sulfur dioxide was observed during the second stage, especially after the temperature of the sample was raised above 500° C. Magnetic properties of the roast material diminished markedly as the second stage progressed, indicating that the lower valency iron oxides were being oxidized to higher state. Also, the ore turned from the dark brown color prevailing at the end of the first stage to ferric-oxide red at the end of the second.

Although the recovery of copper and nickel in soluble form increased during the second stage, the recovery of iron reached its peak during the first stage and diminished during the second. The decomposition of iron sulfate begins at about 170° C., equation (18), but the basic sulfate is formed which does not fully decompose until heated to 500° to 560° C., equation (20).

In some tests, copper recovery of 100 percent was achieved at the end of the second-stage roast. Nickel recovery, however, reached only 57 percent at the end of the second stage of test 12, as shown in table 4.

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[21] Work cited in footnote 14.

Third Stage of Roasts

The objective of the third stage of the roasts was to complete the decomposition of soluble iron sulfate into the less soluble ferric oxide and to increase the water solubility of copper and nickel to satisfactory levels. Copper recoveries approached the maximum attainable, but nickel recoveries were less satisfactory, varying from 55 to 72 percent in tests 10, 11, and 12. Recovery of iron varied from 2.0 to 3.9 percent for the same tests. In test 1, which was not given a third-stage roast, 13.1 percent of the iron was recovered in the final leach solution.

The temperature range of 590°-600° C. appears to be satisfactory for the third stage of the roast. At this temperature range, copper sulfate suffers little or no decomposition during the time required to decompose most of the remaining iron sulfates into ferric oxide and sulfur trioxide. Also, the solubility of nickel is improved during this stage through continued sulfatization. Further improvement of nickel recovery might possibly be effected by increasing the partial pressure of sulfur trioxide in the atmosphere during the third stage. This condition should accelerate the reaction:

$$NiO + SO_3 \rightarrow NiSO_4.$$

Also, alternate grinding and roasting might effect increased nickel recovery by continuously breaking down the protective oxide shells that Thornhill and Pidgeon[22] found to occur when roasting pentlandite. Klyachko-Gorvich[23] and associates accomplished complete sulfatization of nickel oxide by repeatedly pulverizing the compounds in the presence of mixtures of sulfur dioxide and oxygen, which further supports the probability of improving nickel recovery by additional grinding of the leach residue followed by another roast-leach operation. Samples subjected to a fourth-stage roast at 700° C. (tests 9 and 11) showed iron solubilities of only 1.2 and 0.2 percent, respectively; however, solubility of copper was lowered. The solubility of nickel was also lowered by the fourth-stage roast in test 9, but was increased in test 11.

Miscellaneous Roasts

At the end of roasting stage one, test 13, the ore dish was covered and the test was completed through stages two and three without the ore being rabbled or exposed to air. No samples were taken from the termination of stage one to the end of the test. The recovery of iron was 3.2 percent, while the recovery of copper and nickel was considerably lower than expected, 58.4 and 27.8 percent, respectively. This lowering of copper and nickel recovery may be partly explained by elimination of the oxidation reaction during the second and third stages because of the exclusion of air and not rabbling. On the other hand, increased recovery of copper and nickel might be expected because of the increase in partial pressure of sulfur trioxide, which would be retained in the covered dish and held in contact with the sample in greater concentration for longer time.

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[22] Work cited in footnote 8.
[23] Work cited in footnote 15.

OTHER INVESTIGATIONS

Roasting

Samples of Funter Bay ore were roasted to reduce the sulfur content to proper level for production of matte by smelting and for other testing purposes, such as leaching. Because the conventional multiple-hearth furnace that would normally be used for roasting sulfide ores was not available, rotary kilns of laboratory and pilot plant size were employed. Also a single-hearth laboratory-size furnace was used for some dead-roasting runs. Small batches of ore were roasted in an iron-tube kiln, 6 inches in diameter by 12 feet in length, with automatically controlled externally heated zones. Larger amounts of both lot 1 and lot 2 ores were roasted in a 15-foot pilot plant rotary kiln, 18 inches in diameter, at temperatures up to 900° C. To avoid matting and burning of the ore from overheating, the temperature was carefully controlled and the kiln was tilted to effect rapid passage of ore through the hot zone. From four to five passes of the ore were required to reduce sulfur content to an amount, about 10 percent, that would permit matte smelting. The coarse size of the ore, minus 8-mesh, retarded the rate of roasting and, therefore, the ore was passed through a hammermill after the third and fourth passes to break up the roasted outer layers and expose new sulfide surfaces.

The sulfur content of roasted materials varied. The product of a roast of raw ore in the laboratory-size kiln showed sulfur content of 7.4. Raw ore that was roasted in the pilot plant rotary kiln contained 11.2 and 9.6 percent sulfur at the conclusion of the respective runs. A batch of roasted ore rerun through the pilot plant kiln contained 1.0 percent sulfur. The sulfur in ore given dead-roast treatment in the single-hearth furnace was reduced to 0.4 percent. Table 5 shows the operating conditions and results of various roasts.

Matte Production

Electric Smelting of Roasted Sulfide Ores

The roasted head samples of Funter Bay ore were smelted in the electric furnace to separate copper, nickel, and iron sulfides from the gangue. The sulfides, which are mutually soluble in molten state, form a layer on the hearth in which the molten slag, composing the upper layer, is insoluble. A small, single-phase electric-arc furnace of about 100-pound capacity was used in the matte smelting operations. A highly acid bath was maintained during melting, using current of about 1,500 amperes at 60 volts. There was little attrition of the furnace lining and little electrode consumption. When the smelting operation was completed, the entire batch was tapped into a crucible where the slag and matte separated into their respective layers. Results of two typical matte smelting tests are shown in table 6. Copper content increased from 3.6 percent in the charges to 13.5 percent average in the matte, while nickel content increased from 1.95 percent in the charge to 10.25 average in the matte. Fluxing of iron oxide from the charge into the slag reduced the iron content from 60.9 in the charge to a range of 55.9 to 56.5 percent in the matte. Sulfur content increased from 10.6 percent in the charge to 20.3 to

21.2 percent in the matte. The sulfur contents of the mattes were lower than the theoretical quantities, assuming that the metals present were in sulfide form. This stoichiometric imbalance between sulfur and metals was probably the result of slag entrainment in the mattes, which resulted from rapid chilling of the small batches produced and insufficient time being allowed for complete separation of the slag and matte layers.

TABLE 5. - Roasting tests

	1	2	3	4
Rotary kiln used	Small	Large	Large	Large
Charge material:				
Source	Lot 1	Lot 1	Lot 2	([1])
Total weight, lb	503	2,872	14,129	8,699
Screen size, mesh	-20	-8	-	-
Analysis, percent:				
Copper	3.1	3.1	3.2	-
Nickel	1.9	1.9	1.6	-
Iron	54.5	54.5	48.2	-
Sulfur	32.8	32.8	35.6	-
Roasting temperature, °C.:				
Zone 1	550	365	350	500
Zone 2	600	-	-	-
Zone 3	700	-	-	-
Zone 4	800	900	900	950
Roasted product:				
Total weight, lb.:				
First pass	[2]435.5	2,490	-	6,094
Second pass	[3]147.0	2,432	-	-
Third pass	[3]140.0	2,199	-	-
Fourth pass	121.5	2,175	10,247	-
Fifth pass	-	1,993	-	-
Analysis, percent:				
First pass: Sulfur	18.0	28.4	22.9	-
Second pass: Sulfur	12.6	26.8	20.1	-
Third pass: Sulfur	8.6	21.0	[3]14.6	-
Fourth pass: Sulfur	7.4	[5]14.8	[3]9.6	-
Fifth pass: Sulfur	-	[5]11.2	-	-
Final product:				
Copper	3.1	3.4	3.3	3.4
Nickel	2.2	2.2	1.6	1.6
Iron	61.8	62.9	52.4	52.6
Sulfur	7.4	11.2	9.6	1.0

[1] Charge was composed of raw ore and ore previously roasted to 6.23 percent S.

[2] Ten pounds removed for sample; 7 pounds nodules removed.

[3] Ten pounds removed for sample.

[4] Ore crushed before 3d and 4th passes.

[5] Ore crushed before 4th and 5th passes.

TABLE 6. - Electric smelting of roasted ore for matte production

	Test	
	1	2
Charge material:		
Ore:		
Weight, lb	100	100
Analysis, percent:		
Copper	3.60	3.60
Nickel	1.95	1.95
Iron	60.9	60.9
Sulfur	10.6	10.6
Coke, lb	-	0.5
Silica, lb	25	25
Matte produced:		
Total weight, lb	16.0	13.0
Analysis, percent:		
Copper	13.4	13.6
Nickel	10.2	10.3
Iron	56.5	55.9
Sulfur	21.2	20.3
Total	101.3	100.1
Slag produced:		
Total weight, lb	105.0	96.0
Analysis, percent:		
Copper	1.0	1.5
Nickel	0.4	0.5
Iron	49.0	51.3
Sulfur	3.6	4.5
Distribution, percent:		
In matte:		
Copper	59.4	49.2
Nickel	83.6	68.7
Iron	14.8	11.9
Sulfur	32.0	24.9
In slag:		
Copper	28.1	39.4
Nickel	21.5	24.6
Iron	84.5	80.9
Sulfur	35.9	40.6

Electric Smelting of Oxidized Ore With Sulfide Ore Additions

Smelting tests were made using nonsulfur-bearing nickel silicate ore from Nickel Mountain, Riddle, Oreg., with calculated proportions of Funter Bay sulfide ore to produce sulfide matte. A silica hearth was used to smelt three 100-pound batches of the Nickel Mountain ore to which 3.5, 5, and 7 pounds, respectively, of sulfide ore were added. The excess sulfur contained in the pyrrhotite and pyrite content of the sulfide ore combined with nickel in the nonsulfur ore, forming nickel sulfide, which together with the copper, nickel, and iron sulfides in the Funter Bay ore, formed the matte. The silica content of the Nickel Mountain ore was sufficient to provide a highly acid slag and flux the iron oxide into the slag layer. The mattes contained excess metal, in relation to sulfur content, which was probably caused by slag entrainment in the quickly cooled smelt. Better separation of matte and slag layers could be expected in larger operations. Results of these matte smelting tests are shown in table 7. Although copper and nickel recoveries were low, the mattes would be suitable for the production of low-iron copper-nickel mattes in converters in which the iron sulfide is changed to iron oxide, which is fluxed with silica.

TABLE 7. - Electric smelting of nonsulfide ore with sulfide ore for matte production

	Test		
	1	2	3
Charge material, lb.:			
Riddle nickel ore	100	100	100
Funter Bay ore	3.5	5	7
Composite analysis ores charged, percent:			
Copper	0.11	0.15	0.20
Nickel	1.22	1.22	1.22
Iron	11.9	12.5	13.1
Sulfur	1.22	1.71	2.34
Matte produced:			
Total weight, lb	2	3	3
Analysis, percent:			
Copper	1.94	2.82	3.50
Nickel	27.2	23.7	24.4
Iron	52.9	48.9	47.6
Sulfur	12.5	13.1	14.5
Total	94.5	88.5	90.0
Slag produced:			
Total weight, lb	83	87	87
Analysis, percent:			
Copper	0.06	0.06	0.06
Nickel	0.40	0.32	0.35
Iron	12.4	11.3	12.2
Sulfur	1.51	1.88	1.72
Recovery in matte, percent:			
Copper	34.0	53.7	49.1
Nickel	43.2	55.5	56.1

Chlorinating

Tests were made to explore the possibility of separating the metallic constituents of Funter Bay ore by means of direct chlorination and selective condensation of the nickel, copper, and iron chlorides. Samples of ground ore were pelletized and chlorinated at temperatures ranging from 450° to 600° C. Good recovery of nickel in the residue with relatively low contamination by iron was achieved at 500° C. Best recoveries in the residue were, in percent: nickel, 94.8; copper, 2.9; and iron, 0.99. The residue contained, in percent:

nickel, 20.3; iron, 6.3; and copper, 1.06. Although the tests conducted showed that chlorination might be practicable for separating copper and nickel from the ore, the high iron content resulted in excessive consumption of chlorine. For this reason, chlorination does not appear to be advantageous when projected into commercial application. This avenue of research was not further explored.

Leaching

Leaching tests were performed on raw and roasted Fanter Bay ore to determine feasible means of extracting the copper and nickel values. Roasting treatments made on the ore before leaching included: Simple roasting to reduce excess sulfur; dead roasting to remove all sulfur; sulfatizing roasting to convert the mineral sulfides to sulfates; and roasting with added sodium chloride, sodium carbonate, and sodium chloride plus sodium carbonate. Leaching solutions used were water and aqueous solutions of NH_4OH, H_2SO_4, Na_2CO_3, $(NH_4)_2SO_4$, NaCl, NH_4OH plus Na_2CO_3, NH_4OH plus SO_2, NH_4OH plus Na_2CO_3 plus SO_2, Na_2CO_3 plus SO_2, Na_2CO_3 plus NaCl, and NH_4OH plus NaCl.

Some leaching tests were performed in laboratory-scale equipment that could be used as a six-stage continuous leaching device or as six individual single-stage units. The six tubes, each capable of holding 250 grams of ore, were held in a frame. Under each ore column was a beaker of leach solution. An airlift continuously carried the solution to the top of the ore column and could be used to recirculate the solution continuously to the same ore column or advance the solution to the next ore column.

Except for water leaching of sulfatized ore, none of the leaching tests performed appeared to hold promise for commercial application. The results of the six-stage water leach of raw ore, which is an adaptation of the now nearly obsolete heap leaching process, showed that appreciable quantities of nickel were dissolved, but only traces of copper were recovered. Leaching dead-roasted ore with sulfuric acid effected recoveries approaching 60 percent for both copper and nickel, but the overall results do not appear to have practical significance.

CONCLUSIONS AND RECOMMENDATIONS

To prevent excessive loss of nickel values, which are closely associated with pyrrhotite, maximum beneficiation of the ore is limited to separation of gangue from total sulfides. This separation can be achieved by total sulfide flotation followed by magnetic separation of the tailings.

Sulfatizing roasting and subsequent leaching of the ore with water or dilute sulfuric acid was the only test method among those tried which appeared promising for commercial application.

Maintaining the proper time temperature relationship and atmospheric conditions during the various stages of sulfatizing roasting is of paramount importance in obtaining high copper and nickel and low iron recoveries. Very fine grinding of the concentrate is required for best nickel recovery.

Scaled-up investigations on these ores, using a fluid-bed reactor, would be desirable. This type of equipment might prove useful in exploiting relatively small and widely separated cupriferous and nickeliferous pyrrhotite deposits that occur in Alaska and the Pacific Northwest. Also, further studies may develop techniques for increasing recovery of nickel from nickeliferous pyrrhotites to a level that would be more attractive for commercial application.