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Recovery of Copper From Granulated Blast Furnace Slag

By C. E. Jordan, G. V. Sullivan, and E. D. Scott

UNITED STATES DEPARTMENT OF THE INTERIOR
Cecil D. Andrus, Secretary

BUREAU OF MINES

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RECOVERY OF COPPER FROM GRANULATED BLAST FURNACE SLAG

by

C. E. Jordan,[1] G. V. Sullivan,[2] and E. D. Scott[3]

ABSTRACT

The Bureau of Mines conducted bench- and small-scale continuous studies to develop a process for recovering a recyclable copper product from waste, granulated, blast furnace slag. The investigation was part of the Bureau's secondary resource recovery program. The slag contained 5 to 7 percent total copper, of which 3 to 4.5 percent was metallic copper. Tabling of the slag, ground through 35 mesh, recovered 58 percent of the total copper and 88 percent of the metallic copper in a concentrate that contained 39 percent copper. Flotation of the slag, ground through 65 mesh using a xanthogen formate collector, produced a concentrate containing 32 percent copper and recovered 76 percent of the total copper and 98 percent of the metallic copper.

A small-scale continuous test was conducted to investigate simple gravity-separation techniques. A 40-hour test was made with a circuit that included rod mill grinding, a Humphreys spiral, and shaking tables. Two concentrates were prepared according to particle size; the plus 35-mesh concentrate contained 68 percent copper, and the minus 35-mesh concentrate contained 72.5 percent copper. The composite of the copper products contained 70 percent copper; the process recovered 60 percent of the total copper and 90 percent of the metallic copper.

INTRODUCTION

To maintain an adequate supply of minerals to meet national and strategic needs, the Bureau of Mines devotes a portion of its research to maximizing metal recovery from secondary domestic resources, including industrial wastes. As a part of this secondary resource recovery program, the Tuscaloosa Metallurgy Research Center made preliminary studies of secondary copper blast furnace slag samples submitted by Copper Div., Southwire Co., Carrollton, Ga.

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The slag samples were from blast furnace smelting of low-grade copper scrap and in-house waste from other furnacing operations. A portion of this type of slag is cast and recycled to the furnace, but most is granulated and discarded.

The Bureau has studied the recovery of copper from converter slags.[4] Copper in converter slag is usually found as sulfides, but in the secondary copper blast furnace slag, both metallic and oxide copper are present. The cooperating company indicated that a copper concentrate made from the copper blast furnace slag must have a minimum grade of 30-percent copper to justify recycling it to the blast furnace. Preliminary studies were conducted, employing mineral processing techniques, to develop a technically feasible method of recovering copper from secondary copper blast furnace slag. Based on results of these studies, a method was devised and tested on a larger scale continuous unit. This report describes the test results from the batch testing and from the continuous unit.

ACKNOWLEDGMENTS

The authors wish to thank the Copper Div., Southwire Co., Carrollton, Ga., for furnishing all slag samples used in this research and for funding the continuous testing under cooperative agreement 14-09-0070-559.

DESCRIPTION OF MATERIAL

Two samples of granulated copper blast furnace slag were received from the Copper Div., Southwire Co.; analyses of these samples are shown in table 1. Both slag samples were black with a typical glassy appearance. A 50-pound grab sample from the waste-slag pile, which contained 4.05 percent metallic copper and 2.69 percent oxide copper, was used for the batch testing. A 20-ton grab sample for continuous-process testing contained 3.01 percent metallic copper and 1.87 percent oxide copper.

TABLE 1. - Analyses of slag samples

Slag	Analysis, percent			
	Metallic copper	Oxide copper	Total copper	Iron
50-pound sample.	4.05	2.69	6.74	18.2
20-ton sample...	3.01	1.88	4.89	26.2

Oxide copper content was determined by treating minus 200-mesh material in 15 percent sulfuric acid for 1.5 hours at room temperature. Copper that dissolved was considered to be oxide. Metallic copper content was determined as the difference between total copper and oxide copper, although some micrometer-size metallic copper may dissolve and be reported as oxide copper. For samples in which the metallic copper would not grind to minus 200 mesh, the metal fraction was analyzed separately by the same procedure, and analysis of the original sample was calculated.

[4]Edlund, V. E., and S. J. Hussey. Recovery of Copper From Converter Slags by Flotation. BuMines RI 7562 (rev.), 1972, 12 pp.

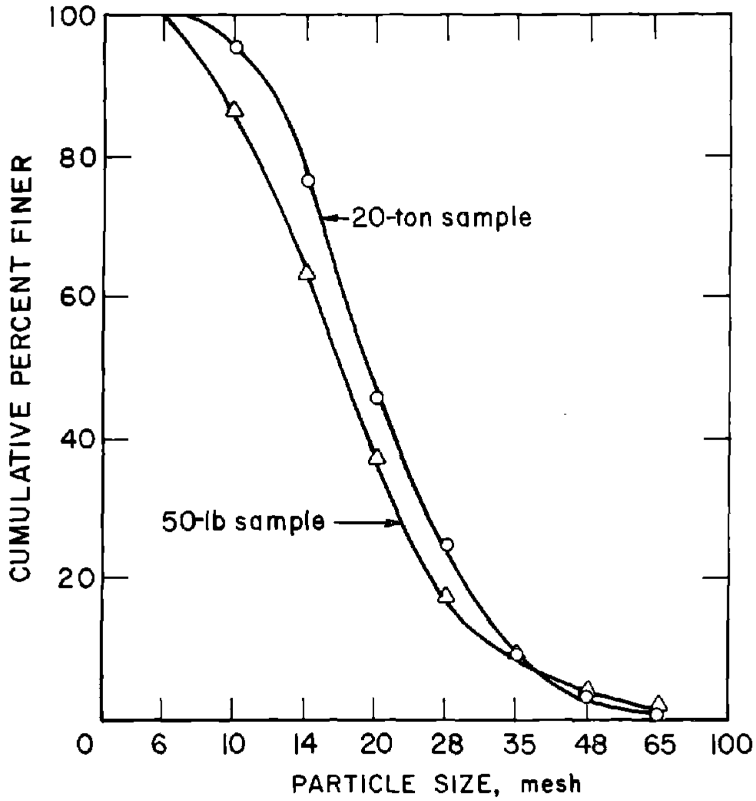

FIGURE 1. - Size distribution of slag samples.

Both slag samples had similar size distributions, as shown in figure 1. Table 2 shows the analyses of each sized fraction. Examination of the sized fractions showed the presence of free metallic copper in all fractions and essentially complete liberation of the metallic copper in the minus 35-mesh fractions. X-ray diffraction analysis of the slags revealed only the presence of metallic copper. The remaining material was amorphous and could not be identified by X-ray diffraction. The oxide copper is probably uniformly dispersed throughout the slag so that a high recovery of the oxide copper by any physical separation process is unlikely. Only the metallic copper was found as discrete grains within the slag particles.

TABLE 2. - Size and copper distribution analyses of slag samples

Slag sample	Weight-percent	Copper analysis, percent			Copper distribution, percent		
		Metal copper	Oxide copper	Total copper	Metal copper	Oxide copper	Total copper
Granulated slag, 50-pound sample:							
Plus 10 mesh.......	4.1	5.50	2.83	8.33	5.5	4.3	5.1
Minus 10 plus 20...	50.0	4.18	2.63	6.81	51.6	48.9	50.5
Minus 20 plus 35...	36.7	3.31	2.68	5.99	30.0	36.6	32.6
Minus 35 plus 48...	6.2	6.13	2.81	8.94	9.4	6.5	8.2
Minus 48 plus 65...	2.6	5.03	3.24	8.27	3.2	3.1	3.2
Minus 65 mesh......	.4	2.62	4.33	6.95	.3	.6	.4
Composite.......	100.0	4.05	2.69	6.74	100.0	100.0	100.0
Granulated slag, 20-ton sample:							
Plus 10 mesh.......	12.8	1.73	1.73	3.46	7.4	11.9	9.1
Minus 10 plus 20...	49.9	2.12	1.78	3.90	35.1	47.5	39.8
Minus 20 plus 35...	28.7	3.34	1.97	5.31	31.8	30.2	31.2
Minus 35 plus 48...	4.5	9.41	2.09	11.50	14.0	5.0	10.6
Minus 48 plus 65...	2.2	11.20	2.24	13.44	8.2	2.6	6.0
Minus 65 mesh......	1.9	5.62	2.76	8.38	3.5	2.8	3.3
Composite.......	100.0	3.01	1.87	4.89	100.0	100.0	100.0

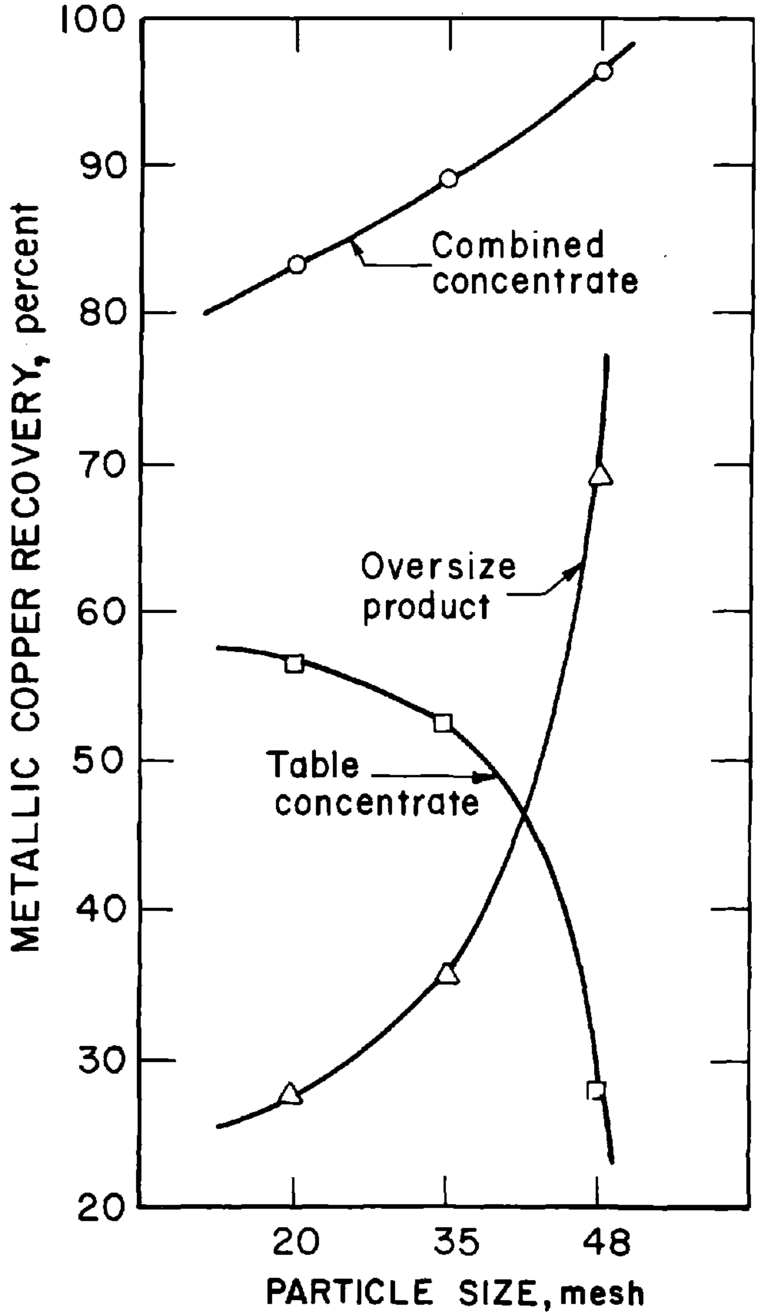

FIGURE 2. - Metallic copper recovered by tabling compared with grinding.

BATCH BENEFICIATION STUDIES

Gravity Concentration

Tabling tests were conducted to determine the amenability of the metallic copper to gravity concentration. Some grinding of the slag was necessary to liberate the metallic copper. The test samples were wet-ground in a ball mill and screened, in stages, until the bulk of the oversize material was metallic copper. Individual samples were ground to various degrees, through 20 mesh, 35 mesh, or 48 mesh. The undersize material of each test, when tabled on a laboratory shaking table, yielded concentrates containing 20 to 39 percent copper. The table concentrate and the oversize material were combined to form the composite copper concentrate. Table 3 shows the recovery of these concentrates to be 55 to 70 percent of the total copper and 83 to 96 percent of the metallic copper.

The effect of grinding on metallic copper recovery by gravity concentration is shown in figure 2. As the mesh of grind was increased from 35 to 48 mesh, the amount of metallic copper recovered in the oversize product increased sharply. Although the amount of metallic copper recovered by the tabling operation dropped sharply, the combined concentrate still experienced a steady increase in metallic copper recovery. Since the grinding process is generally more expensive than the tabling operation, the degree of grinding should be kept to a minimum. The optimum degree of grinding was found to be 35 mesh, which produced a combined concentrate containing 39 percent copper, and 88 percent of the metallic copper and 58 percent of the total copper were recovered.

TABLE 3. - Tabling test on granulated slag

Particle size	Copper analysis, percent			Combined concentrate recovery, percent	
	Oversize product	Table product	Combined concentrate	Total copper	Metallic copper
20 mesh.......	81.0	15.6	20.0	55.4	83.4
35 mesh.......	81.4	29.6	39.4	57.8	88.0
48 mesh.......	88.7	12.8	28.7	69.9	95.6

Flotation

The flotation of metallic copper is a well-established process, and several successful copper flotation processes have been developed for treating native copper ores and converter slags. The general method used to treat the slag samples in the present investigation was as follows: A 500-gram sample was wet-ground in a ball mill in 5- to 10-minute stages and screened to remove the undersize material until the bulk of the oversize material was metallic copper. The undersize material was conditioned in the flotation cell with a collector for 5 minutes. The slurry was floated for 2 minutes with a frother at natural pH. The pulp was reconditioned and floated twice, producing two scavenger concentrates and a tailings product. The three flotation concentrates and the oversize product were combined to form a copper concentrate.

Grinding of the slag was necessary to liberate the metallic copper particles and to facilitate bubble pickup of the particles during flotation. Three samples of the granulated slag were ground through 48, 65, and 100 mesh, to determine the optimum grinding size. For sizes coarser than 65 mesh, the metallic copper recovery of the flotation process decreased sharply; for sizes finer than 65 mesh, the metallic copper recovery increased only slightly. This trend, shown in figure 3, indicates that the optimum grinding size for the flotation process is 65 mesh.

Two xanthate collectors and a xanthogen formate collector were tested at various levels in these flotation studies. One-third of the total reagent was used for each rougher and scavenger float. Potassium ethyl xanthate at 0.3 pound per ton, sodium ethyl xanthate at 0.3 pound per ton, and the xanthogen formate at 0.6 pound per ton produced the best grades and recoveries of the copper concentrate. The results are shown in table 4. The oxide copper was not effectively recovered in the copper concentrate; however, the xanthogen formate collector recovered more of the oxide copper than either of the xanthate collectors. Aside from this minor difference, all three reagent schemes produced similar product grades and recoveries. The optimum reagent scheme would depend only on the cost of the reagents.

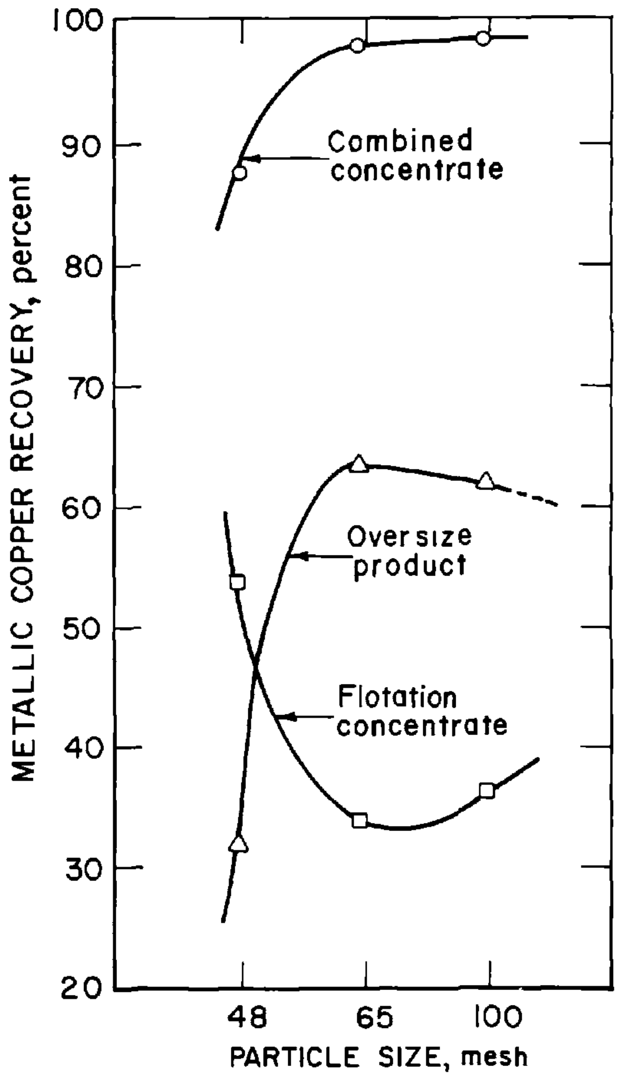

FIGURE 3. - Metallic copper recovered by flotation compared with grinding.

TABLE 4. - Flotation concentrates for each reagent scheme[1]

	Reagent		
	K-ethyl xanthate	Na-ethyl xanthate	Xanthogen formate
Pound per ton	0.3	0.3	0.6
Copper analysis:			
Metallic copper...percent..	29.0	27.1	28.9
Oxide copper...do....	2.8	2.9	3.2
Total copper...do....	31.8	30.0	32.1
Copper distribution:			
Metallic copper...percent..	95.0	96.6	97.9
Oxide copper...do....	17.5	18.8	24.3
Total copper...do....	68.2	69.2	75.5

[1]Slag ground to 65 mesh.

Results of a typical flotation test are shown in table 5. Seventy-four percent of the metallic copper was recovered in the oversize product. Twenty percent of the metallic copper was recovered in the rougher float, but only 4 percent of the metallic copper was recovered in the two scavenger floats combined.

TABLE 5. - Flotation with xanthogen formate collector

Product	Weight-percent	Copper analysis, percent			Copper distribution, percent		
		Metallic copper	Oxide copper	Total copper	Metallic copper	Oxide copper	Total copper
Plus 65 mesh............	5.0	80.6	1.25	81.8	73.9	2.6	52.2
Rougher concentrate[1]....	8.0	13.8	4.42	18.2	20.3	14.8	18.6
Scavenger concentrate 1[1]	4.2	4.7	3.12	7.8	3.6	5.5	4.2
Scavenger concentrate 2[1]	1.2	.56	2.92	3.5	<.1	1.4	.5
Combined concentrate....	18.4	28.9	3.16	32.1	97.9	24.3	75.5
Tailings[1]...............	81.6	.14	2.22	2.36	2.1	75.7	24.5
Composite..........	100.0	5.4	2.39	7.8	100.0	100.0	100.0

[1]Flotation feed ground through 65 mesh.

A cleaner concentrate containing 15 percent copper was floated from the combined rougher and two scavenger concentrates with no additional reagents. The cleaner concentrate and the oversize products were combined to make a concentrate containing 34 percent copper. The total copper recovery was 75 percent. In a continuous process, the cleaner tailings would be recirculated to the rougher flotation step.

Discussion of Beneficiation Processes

Both flotation and gravity concentration resulted in products of suitable copper grades and recoveries for recycling to the copper blast furnace. The additional grinding expense necessary for flotation appears to be compensated by the added copper recovery. The cooperative company planned to treat about 5 tons per hour of granulated slag and preferred the simpler gravity-concentration method. Continuous gravity-concentration studies were initiated to demonstrate the effectiveness of this method. Continuous flotation studies and an economic comparison of the two processes was beyond the scope of this research.

CONTINUOUS PROCESS DEVELOPMENT UNIT TESTS

Table-Spiral Circuit

A continuous unit was designed that incorporated a table-spiral circuit based on the results of the preliminary beneficiation studies. The circuit, illustrated in figure 4, included a spiral to increase the processing rate.

Approximately 20 tons of granulated copper blast furnace slag was screened at 6 mesh to remove the yard scrap and oversize material. The minus 6-mesh material was thoroughly mixed, coned, quartered, and sampled for

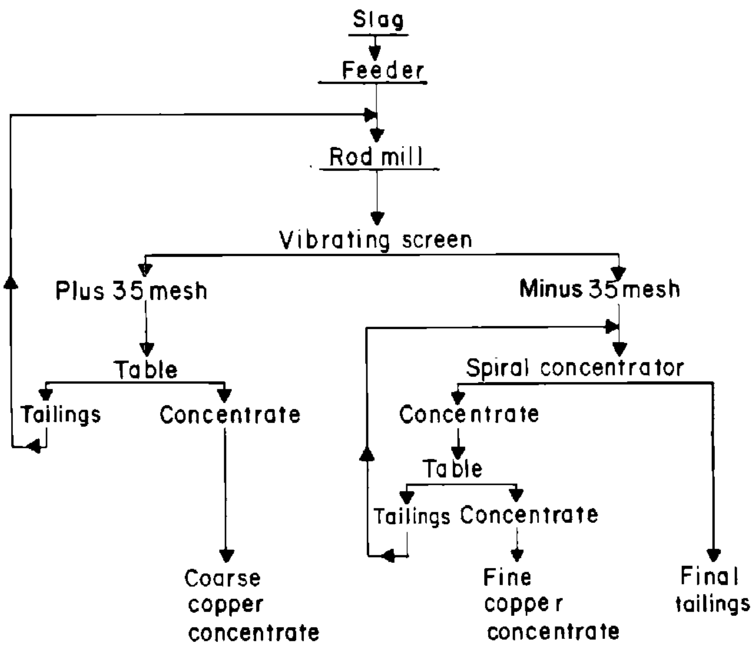

FIGURE 4. - Flowsheet for table-spiral circuit.

chemical analyses. A representative sample of the slag contained 3.0 percent metallic copper and 1.9 percent oxide copper.

The minus 6-mesh slag was fed at a rate of 250 to 300 pounds per hour to a peripheral discharge rod mill, 18 inches inside diameter by 4 feet long. The peripheral discharge mill would allow the large pieces of malleable copper to be readily discharged from the mill onto a 35-mesh vibrating screen. The plus 35-mesh material was fed to a small Wilfley[5] concentrating table; a coarse copper concentrate was yielded and the tailings were returned to the rod mill for regrinding. The minus 35-mesh material was fed to a five-turn Humphreys spiral. The spiral separation was designed to produce a low-grade-copper concentrate with high recovery of the metallic copper and thus relieve the load on the table. The spiral tailings were dewatered in a screw classifier and removed from the circuit as a final tailings product. The spiral concentrate was fed to a small Diester concentrating table, where a fine copper concentrate was produced. The Diester table tailings were recirculated to the spiral feed. Throughout the circuit, the slurry was transported by vertical sand pumps. At various points in the circuit, water was added to the slurry to aid the pumps in moving the material. Generally, this excess water was removed prior to entering the next unit operation; however, the water was not removed before the slurry entered the spiral and the vibrating screen.

[5]Reference to specific makes and models of equipment is made for identification purposes only and does not imply endorsement by the Bureau of Mines.

This circuit was operated continuously, 8 hours per day for 5 days. The coarse and fine concentrates contained 68 and 72.5 percent copper, respectively; the process recovered 60 percent of the total copper and 90 percent of the metallic copper. Summarized results of the test are shown in tables 6 and 7. The feed rate ranged from 250 to 300 pounds per hour with an average rate of 275 pounds per hour. Sampling during operation revealed that the copper analysis of the feed ranged from 4.1 percent to 6.3 percent, with an average of 4.9 percent of total copper. The metallic copper analysis of the feed varied with the total copper analysis, but the oxide copper analysis remained fairly constant at about 2 percent. The coarse concentrate showed wide variation in the flow rates and copper analyses, ranging from 2 to 6 pounds per hour and 55 to 84 percent copper, respectively. This was due to the fluctuations in the discharge rate of the plus 35-mesh material from the vibrating screen. The fine-copper concentrate showed very little variation in flow rate, ranging from 6.2 to 6.6 pounds per hour; the copper content ranged from 67 to 76 percent, with an average of 72 percent copper. The flow rate of the final tailings varied with the feed rate, ranging from 240 to 290 pounds per hour, but analyses of this product remained 2.00 to 2.09 percent total copper and 0.31 to 0.40 percent metallic copper. Thus, despite the wide fluctuations of the feed and the coarse concentrate, the total copper recovery and the metallic copper recovery remained fairly constant at 60 and 87 percent, respectively.

TABLE 6. - Results for table-spiral circuit

	Coarse copper concentrate	Fine copper concentrate	Tailings	Composite	Combined concentrate
Weight-percent..................	1.9	2.3	95.8	100.0	4.2
Copper analysis:					
Metallic copper.......percent..	67.3	72.0	.34	3.26	69.9
Oxide copper............do....	.69	.48	1.70	1.65	.57
Total copper............do....	68.0	72.5	2.04	4.91	70.5
Copper distribution:					
Metallic copper.......percent..	39.2	50.8	10.0	100.0	90.0
Oxide copper............do....	.8	.7	98.5	100.0	1.5
Total copper............do....	26.3	33.9	39.8	100.0	60.2

TABLE 7. - Daily material balance for table-spiral circuit

Product	1st day		2d day		3d day		4th day		5th day		Average	
	Flow rate, lb/hr	Copper analysis, pct	Flow rate, lb/hr	Copper analysis, pct	Flow rate, lb/hr	Copper analysis, pct	Flow rate, lb/hr	Copper analysis, pct	Flow rate, lb/hr	Copper analysis, pct	Flow rate, lb/hr	Copper analysis, pct
Feed........	275	5.0	255	5.0	251	4.6	294	4.8	298	5.1	275	4.9
Rod mill....	475	3.9	482	4.5	272	4.5	338	4.9	387	5.7	391	4.7
Plus 35 mesh	206	4.0	233	5.4	22.9	11.2	51.2	12.3	94.6	12.0	122	9.0
Coarse table concentrate	6.1	54.8	5.6	63.8	2.1	81.7	6.9	55.6	5.4	84.0	5.2	68.0
Coarse table tailings...	200	2.5	227	3.9	20.8	4.2	44.3	5.6	89.2	7.6	116	4.8
Minus 35 mesh.......	269	3.8	249	3.7	249	3.9	287	3.6	293	3.6	269	3.7
Spiral feed.	428	4.6	529	2.9	378	3.6	353	3.5	350	3.3	408	3.6
Spiral concentrate	165	8.7	287	3.6	135	6.3	72.0	9.4	63.1	9.1	144	7.4
Spiral tailings...	263	2.1	243	2.0	242	2.0	281	2.1	287	2.0	263	2.0
Fine table concentrate	6.6	74.5	6.3	66.9	6.6	72.7	6.4	72.2	6.2	76.3	6.4	72.5
Fine table tailings...	158	5.9	280	2.2	129	2.9	65.6	3.3	56.9	1.7	138	3.2

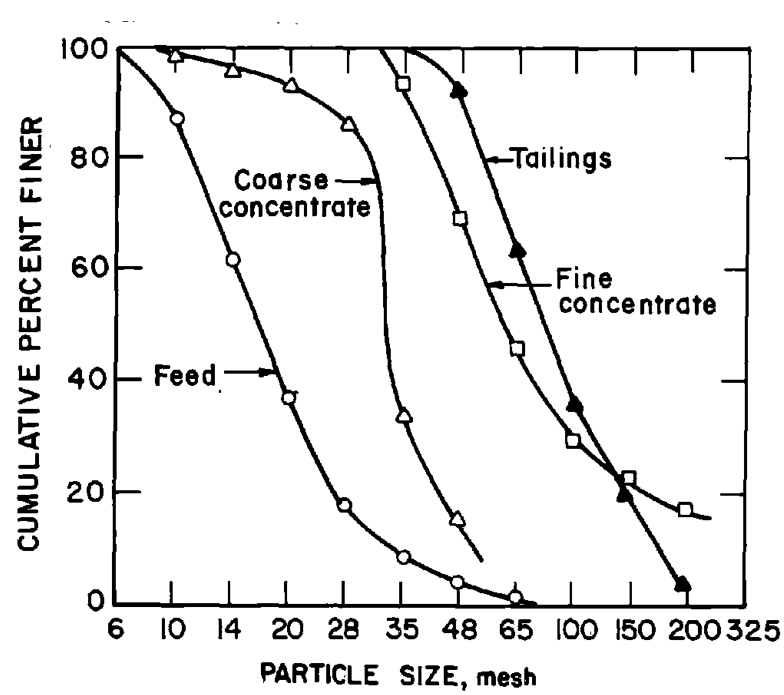

FIGURE 5. - Size distribution of copper products from table-spiral circuit.

The size distributions of the two copper concentrates, the tailings product, and the feed size are shown in figure 5. The copper concentrates would need to be pelletized before recycling to the furnaces. The tailings product could be used as a rounded grit or discarded.

Modified Circuit

A small, 1- by 2-inch mineral jig containing 1/8-inch steel shot was substituted for the coarse concentrating table as shown in figure 6. In an 8-hour test made using this modified circuit, the combined jig and fine table concentrate contained 76.3 percent copper and the process recovered 57 and 89 percent of the total and metallic copper, respectively. Summarized results of this test are shown in tables 8 and 9.

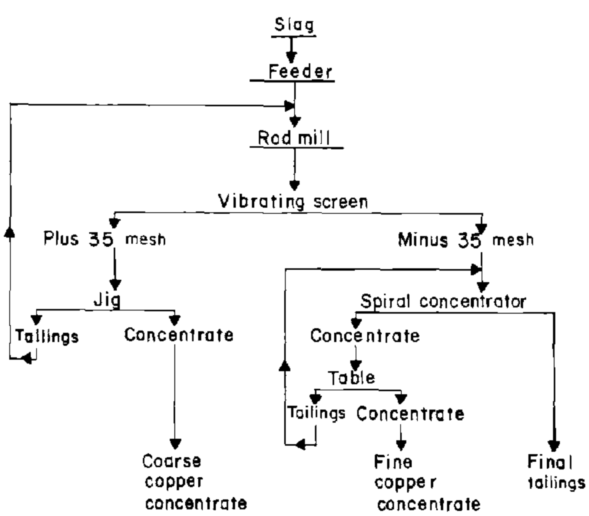

FIGURE 6. - Flowsheet for modified circuit.

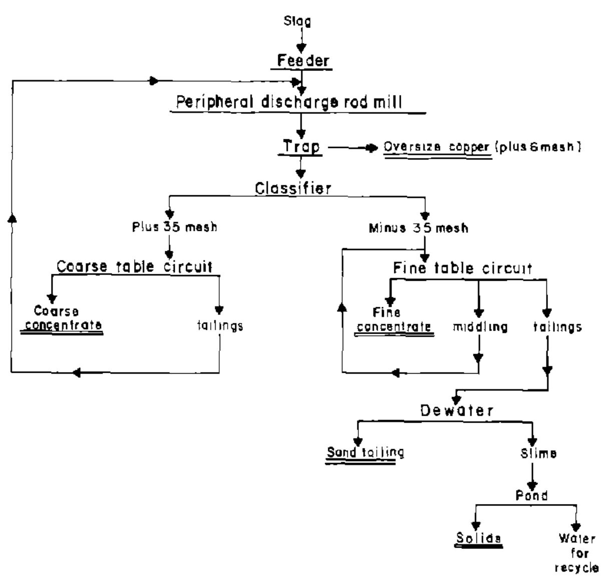

FIGURE 7. - Proposed plant flowsheet.

TABLE 8. - Results for the jig-table-spiral circuit

	Jig concentrate	Table concentrate	Tailings	Composite	Combined concentrate
Weight-percent..................	1.0	2.5	96.5	100.0	3.5
Copper analysis:					
Metallic copper.......percent..	76.2	76.3	.33	2.99	76.3
Oxide copper.............do....	.32	.35	1.77	1.72	.34
Total copper.............do....	76.5	76.7	2.10	4.71	76.6
Copper distribution:					
Metallic copper.......percent..	25.5	63.8	10.7	100.0	89.3
Oxide copper.............do....	.2	.5	99.3	100.0	.7
Total copper.............do....	16.2	40.7	43.1	100.0	56.9

TABLE 9. - Material balance for jig-table-spiral circuit

Product	Flow rate, lb/hr	Copper analysis, percent
Feed................................	261	4.7
Rod mill............................	296	4.7
Plus 35 mesh........................	36.5	9.8
Jig concentrate.....................	2.7	76.5
Jig tailings........................	33.8	4.6
Minus 35 mesh.......................	259	4.0
Spiral feed.........................	417	3.5
Spiral concentrate..................	165	5.7
Spiral tailings.....................	252	2.1
Fine table concentrate..............	6.5	76.7
Fine table tailings.................	158	2.8

The jig produced a more consistent grade of copper in the coarse copper concentrate (about 76 percent). The remainder of the circuit performed similarly to the table-spiral circuit. By decreasing the coarse-copper-concentrate fluctuations, the jig helped to improve the composite copper concentrate to about 76 percent copper without affecting the copper recovery. The slow rate of feed to the jig caused it to operate both as a jig and as a hydraulic classifier. This observation is reinforced by the fact that a bed did not develop in the jig.

Discussion of Generalized Process

A generalized flowsheet of a proposed plant-scale operation is shown in figure 7. Some of the features of this operation are different from the table-spiral circuit of the continuous test work. A trap is placed on the rod mill discharge to remove oversize copper. Although the plus 6-mesh material was not treated in the laboratory tests, it would be treated on a commercial scale. A trap would remove the coarse copper too large to be pumped or tabled. Recovery of the oversize copper would increase the overall recovery of the process.

Although the sizing device for the continuous test work was a screen, any effective classifier could be used. In the generalized flowsheet, the preconcentrating spiral step of the fine copper circuit was replaced with a single tabling operation. This will simplify any operational adjustments needed to maintain grade and recovery. In plant practice, the use of spirals as a rougher concentration mechanism is practical, and the choice would be at the discretion of the plant engineer.

Slime settling and water recycling would be necessary on a plant scale. The slimes settle rapidly with or without flocculant and the use of turbid water would not affect the gravity circuit.

CONCLUSIONS

Bench- and small-scale continuous studies conducted by the Bureau of Mines show the technical feasibility of recovering a recyclable copper product from a waste granulated blast furnace slag. Both gravity separation and flotation on a bench scale produced suitable copper concentrates, containing more than 30 percent copper and recovering more than 60 percent of the copper. Gravity concentration required grinding the ore through 35 mesh; flotation required grinding the ore through 65 mesh.

At the request of Southwire Co., small-scale continuous testing was conducted to develop a simple gravity-separation process. A 40-hour test was made with a circuit that included rod mill grinding, Humphreys spirals, and shaking tables. The copper concentrate contained 70 percent copper, and the process recovered 60 percent of the total copper and 90 percent of the metallic copper.

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15. Supplementary Notes Research at the Tuscaloosa Metallurgy Research Center is carried out under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Alabama.

16. Abstracts
The Bureau of Mines conducted bench and small-scale continuous studies to recover a recyclable copper product from a waste granulated blast furnace slag. The slag contained from 5 to 7 percent total copper, of which from 3 to 4.5 percent was metallic copper. Tabling of the slag ground through 35 mesh recovered 58 percent of the total copper and 88 percent of the metallic copper in a concentrate that contained 39 percent copper. Flotation of the slag ground through 65 mesh using a xanthogen formate collector produced a 32 percent copper concentrate and recovered 76 percent of the total copper and 98 percent of the metallic copper. A small-scale continuous test was conducted to investigate simple gravity separation techniques. A 40-hour test was made with a circuit that included rod mill grinding, a Humphreys spiral, and shaking tables. Two concentrates were prepared according to particle size. The plus 35-mesh concentrate contained 68 percent copper and the minus 35-mesh concentrate contained 72.5 percent copper. The composite of the copper products contained 70 percent copper, and the process recovered 60 percent of the total copper and 90 percent of the metallic copper.

17. Key Words and Document Analysis. 17a. Descriptors

Copper
Beneficiation
Copper slag

17b. Identifiers/Open-Ended Terms

Gravity concentrators
Tables (concentrators)
Spirals (concentrators)
Jigs (concentrators)
Flotation

17c. COSATI Field/Group 11 Materials/F Metallurgy (11/F)

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