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Smelting Cement Copper in an Electric-Arc Furnace

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8284

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By D. L. Paulson, W. Anable, and W. L. Hunter

With an Appendix on Analytical Techniques
by R. F. Farrell and W. J. Niebuhr

UNITED STATES DEPARTMENT OF THE INTERIOR
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SMELTING CEMENT COPPER IN AN ELECTRIC-ARC FURNACE

by

D. L. Paulson,[1] W. Anable,[2] and W. L. Hunter[3]

ABSTRACT

Electric furnace smelting of blister copper directly from copper precipitates (cement copper) was investigated by the Federal Bureau of Mines. Copper concentrations in five different lots of cement copper in the investigation ranged from 62.5 to 82.5 wt-pct.

Laboratory-scale smelting tests were made in a 50-kva electric-arc furnace to establish the reductant and flux requirements. Best recoveries were realized by adding 60 pct of the carbon required to combine with the contained oxygen in the cement copper.

Operating parameters established during the laboratory-scale smelting tests were used successfully in smelting 20 tons of cement copper during 12 pilot-scale tests in an 800-kva electric-arc furnace. Over 98 pct of the contained copper was recovered as blister-grade metal. The projected energy consumption for a commercial-size furnace was 380 kwhr per ton of cold charge.

INTRODUCTION

The production of cement copper has increased steadily because of expanded waste dump leaching programs at many of the open pit mines, recovery of copper from oxide copper deposits, and purification of process streams from many metal-refining industries.[4] Present practices are to smelt cement copper with chalcopyrite concentrates in a reverberatory furnace or to introduce the material into the converting step of a conventional operation. In either case the capacity of the system is limited, and a charge material containing as

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[4] Tilyard, P. Copper Cementation and Its Application in the Leach-Precipitation-Flotation Process. Miner. Sci. and Eng., v. 5, No. 3, July 1973, pp. 192-206.

much as 95 pct copper is processed intimately with a material containing, in many cases, less than 35 pct copper. Because more efficient methods are needed to utilize this significant resource, the Federal Bureau of Mines conducted an investigation to determine the feasibility of producing a blister or anode copper product by smelting cement copper in an electric-arc furnace.

A cyclic process had been developed by Bureau of Mines researchers to recover blister copper from dead-burned copper calcine in an electric furnace.[5] The chemistry of cement copper and results of a previous Bureau of Mines investigation[6] indicates that cement copper would respond to similar treatment. Laboratory and pilot-scale smelting tests were performed to determine if the smelting efficiency, reaction offgas compositions, and product quality would show the process to be compatible with existing operations.

MATERIALS

Five different cement coppers (identified as A through E) were used during the investigation. Copper contents of the materials ranged from 62.5 to 82.5 wt-pct, and all of the as-received cements were about 65 pct minus 100 mesh. The reductants and fluxes used included granulated blast furnace slag that was 100 pct minus 10 mesh and contained 7.72 wt-pct copper. Analyses of the test materials are shown in table 1.

In addition to the chemical analyses, X-ray diffraction analyses were made on cement copper A to determine the compounds of copper present in the material. The initial analysis established the presence of Cu_2O and metallic copper. However, an appreciable amount of the contained copper was associated with an amorphous or crystallite phase that we subsequently attempted to identify by promoting crystal growth without altering the chemical composition of the as-received cement.

Samples of cement copper A were heat-treated under argon in an effort to cause crystallization of the amorphous phase. However, the heat treating did not affect the X-ray diffraction patterns until after oxygen was driven from the system at 1,000° C. A differential thermal analysis of the material from room temperature to 1,000° C did not indicate any phase transformations within the material. Some degree of crystallization was achieved by compacting approximately 100 grams of ground cement copper under 50,000 lb/sq in pressure. The compact was heat-treated at 850° C for 96 hours under vacuum. X-ray diffraction and oxygen analyses of center material from the treated compact

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[5] Hunter, W. L., and W. A. Stickney (assigned to U.S. Department of the Interior). Production of Blister Copper by Electric Furnace Smelting of Dead-Burned Copper Sulfide Concentrates or Copper Oxide Ores. U.S. Pat. 3,857,701, Dec. 31, 1974.

Paulson, D. L., R. B. Worthington, and W. L. Hunter. Production of Blister Copper by Electric Furnace Smelting of Dead-Burned Sulfide Concentrates. 102d AIME Annual Meeting, Chicago, Ill., Feb. 25-Mar. 1, 1973, Paper A73-33, 11 pp.

[6] Brantley, F. E., R. G. Peterson, and J. B. Clemmer. Electric Smelting and Gaseous Refining of Cement-Copper Precipitate. BuMines RI 5899, 1961, 14 pp.

indicated sufficient crystal growth had occurred to identify 65 pct of the material. The oxygen concentration was 10.1 wt-pct (compared with 10.6 wt-pct in the as-received material), and the amount of Cu_2O that could be identified by X-ray diffraction analysis increased to an estimated 52 wt-pct (proportionate to 80 wt-pct of the total sample). The 74.6 wt-pct copper concentration found in the precipitate, if treated as Cu_2O, accounts for a 9.39 wt-pct oxygen concentration, compared with the 10.6 wt-pct oxygen found in the precipitate. Although only 65 pct of the sample could be identified, it was concluded that most of the copper contained in the as-received precipitate was present as Cu_2O.

TABLE 1. - Analyses of test materials, wt-pct

Components	Cement coppers				
	A	B	C	D	E
Copper	74.6	71.7	70.5	82.5	62.5
Iron	3.7	8.63	9.75	6.34	8.19
Zinc	<.1	<.03	.12	.017	.036
Tin	.30	.50	.12	.24	.195
Lead	.33	.16	.10	.21	.12
Nickel	<.1	<.3	.02	.023	.017
Silicon	<1.0	.67	.29	.08	1.04
Aluminum	.4	.38	.67	.35	2.50
Calcium	.1	ND	.22	.04	.14
Sulfur	.5	1.24	.65	.24	1.65
Carbon	.26	ND	.30	.55	.35
Oxygen	10.6	14.7	17.9	9.70	20.5
Silver	.001	ND	Trace	ND	ND
Gold, ppm	3	ND	Trace	ND	ND

	Reductants and fluxes					
	Petroleum coke	Shell carbon	Coke breeze	Silica sand	Cu-bearing slag	Pebble lime
Copper	ND	ND	ND	ND	7.72	ND
Iron	ND	ND	ND	0.01	26.13	ND
SiO_2	ND	ND	ND	99.8	30.9	1.26
Al_2O_3	ND	ND	ND	.11	4.91	.29
CaO	ND	ND	ND	ND	15.0	93.6
MgO	ND	ND	ND	.05	3.98	.42
Sulfur	1.35	0.075	1.09	ND	.27	ND
Carbon	90	98.0	81.0	ND	.22	ND
Volatiles	9	1.39	ND	ND	ND	ND
Ash	.25	.98	ND	ND	ND	ND
Moisture	6	.15	1	ND	ND	ND

ND--Not detected.

ELECTRIC-FURNACE-SMELTING CEMENT COPPER

Smelting Tests in the 50-kva Electric-Arc Furnace

Preliminary smelting tests were made in a laboratory-scale electric-arc furnace. Approximately 35-pound batches of cement copper were smelted to

establish the reductant and flux requirements. After the requirements were determined for one cement copper, cements that contained different amounts of copper were blended with proportionate additives and smelted under the same conditions to compare the copper recoveries.

Materials Used for Smelting Tests in the 50-kva Electric-Arc Furnace

Cement copper A (table 1) was smelted in the first series of the laboratory-scale tests, and subsequent laboratory-scale smelting tests were made on cement coppers B, D, and E to compare the smelting characteristics of the four materials, which had appreciably different compositions.[7] Petroleum coke and coke breeze were used as reductants. In two tests, copper-bearing slag was used as flux in lieu of silica sand.

Equipment and Operating Procedures for Smelting Tests in the 50-kva Electric-Arc Furnace

The single-phase current for the furnace was supplied by a 50-kva welding transformer which was operated from a portable control panel near the furnace. Manually operated rack-and-pinion-mounted electrode clamps controlled the positioning of the 2-inch graphite electrodes. The furnace shell, approximately 17 inches in OD and 17 inches high, was lined with high-purity castable alumina refractory, resulting in a working crucible 12 inches in ID. The crucible was covered with a rammed, high-alumina roof supported by a water-cooled ring. A tap-hole was provided at hearth level to remove the molten product. The furnace and points where offgases were sampled for SO_2 and entrained dust analyses are shown in figure 1. An infra-red gas analyzer was used to monitor the SO_2 levels periodically during each run. The dust sample was collected during each run and was analyzed by atomic absorption and wet chemical techniques.

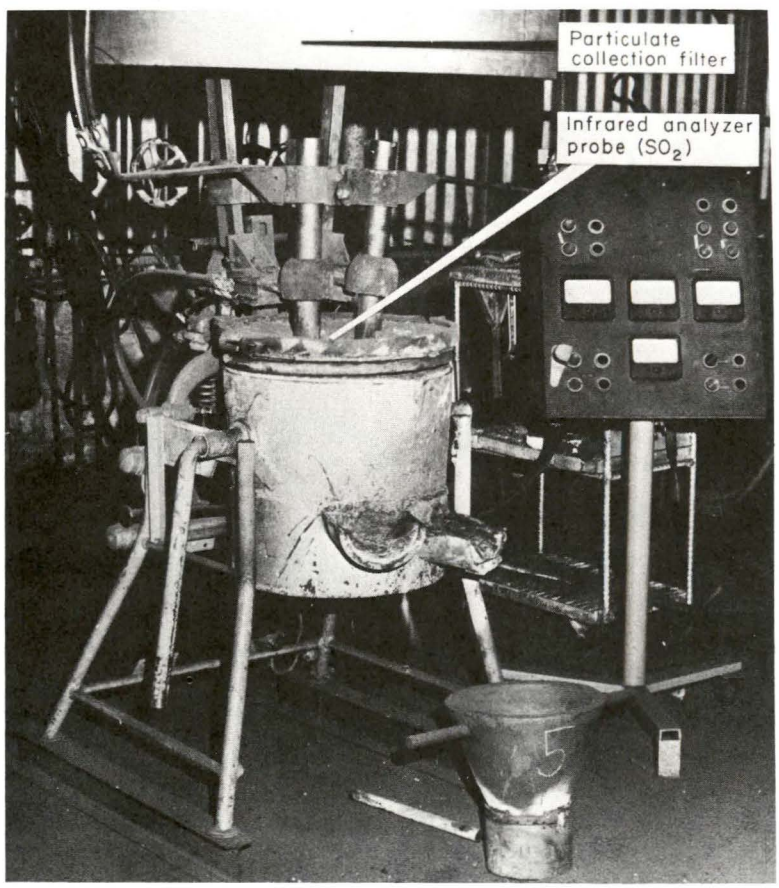

FIGURE 1. - 50-kva electric-arc furnace.

[7] Cement copper C was used in later tests in an 800-kva furnace.

During a test, the blended charge was fed to the furnace with a 4-inch variable-speed belt feeder. The feed rates were correlated with energy input to obtain the desired smelting conditions in the furnace.

To generate the necessary data from the small amount of cement copper E that was available, simulated smelting tests were made on four small (1-pound) batches of the remaining material. The same furnace charge compositions that would be blended for a smelting test in the 50-kva electric-arc furnace were put into mullite crucibles, preheated to 700° C, and transferred to a globar furnace where they were held at 1,300° C for approximately 100 minutes. The simulated smelting conditions produced metal buttons, slags, and amounts of unreacted materials in the same proportions as realized from smelting tests in the 50-kva electric-arc furnace.

Results of Smelting Tests in the 50-kva Electric-Arc Furnace

Twenty-four smelting tests were made to determine the effects of various flux and reductant additions on the smelting of cement copper. The first 10 tests were made on cement copper A to determine the bath composition that provided the best copper recovery and slag fluidity. The rest of the laboratory-scale smelting tests were made on cement coppers B, D, and E to determine if changes in cement composition altered the oxygen-to-carbon ratio in the charge that provided near-optimum conditions for recovery from the original material.

Adjusting the operating conditions to cope with a wide range of furnace bath compositions caused appreciable variations in the operating parameters during the laboratory-scale smelting tests:

Parameter	Range
Bath temperature.....° C..	1,380-1,750
SO_2 content of offgases.....vol-pct..	0.5-4.5
Copper in flue dust.....wt-pct..	57-76

Although some of the bath temperatures were extremely high, a maximum bath temperature of 1,380° C was adequate when the appropriate slag composition was used. When feed rates were constant, the undiluted reaction offgases contained 1 to 1.5 pct SO_2. The flue gases entrained primarily unreacted cement copper.

Emphasis was placed on optimizing copper recovery by varying the chemical composition of the furnace bath. After the first test, silica sand or the equivalent in copper-bearing slag was used in proper portions to the contained iron to form a 1.80 FeO to 1 SiO_2 weight ratio in the slag. Carbon additions were based on the oxygen content of the cement copper. A stoichiometric addition was considered to be the amount of the contained oxygen needed to form CO. Pertinent data from smelting tests in the 50-kva electric-arc furnace are shown in table 2.

TABLE 2. - Data from smelting tests in the 50-kva electric-arc furnace

Test	Charge, lb					Carbon added, pct stoich	Copper recovered as metal, pct	Slag-metal ratio	Electrode consumption, lb
	Cement copper[1]	Silica sand	Coke breeze	Petroleum coke	Slag				
W-1.....	35 A	0	0	0	0	0	67.4	0.38	2.5
W-2.....	35 A	.75	0	0	0	0	47.2	1.1	.75
W-3A.....	35 A	.75	3.97	0	0	120	101.8	.29	1.0
W-3B.....	35 A	.75	1.32	0	0	40	89.1	.13	0
W-4A.....	35 A	.75	2.0	0	0	60	95.2	.04	.5
W-4B.....	35 A	.75	3.31	0	0	100	81.6	.38	.5
W-5A.....	35 A	.75	.62	0	0	20	79.5	.34	.4
W-5B.....	35 A	.75	2.48	0	0	80	92.8	.17	.4
W-6.....	49.2 A	0	2.9	0	1.1	60	95.9	.13	.5
W-7.....	44.8 A	0	2.5	0	20.0	60	[2]97.0	[3].29	1.0
W-8.....	35 B	4.4	2.9	0	0	60	87.5	.30	.9
W-9.....	34.6 D	1.2	0	1.7	0	60	89.7	.03	.4
W-10.....	35 D	1.2	0	1.7	0	60	91.9	.04	.6
W-11.....	35 D	1.54	0	1.13	0	40	86.7	.41	.9
W-12.....	35 D	1.54	0	2.26	0	80	94.8	.07	.6
W-13.....	30 E	1.7	0	3.1	0	60	83.2	.36	.5
W-14.....	30 E	1.7	0	4.1	0	80	90.4	.28	.6
W-15.....	25 E	.9	0	2.6	0	60	90.7	.38	.4
W-16.....	30 D	1.03	0	.51	0	20	93.2	.17	.2
W-17.....	30 D	1.03	0	2.42	0	100	87.0	.10	0
HAR-1[4].....	454 g E	14 g	0	32 g	0	40	96.1	0	0
HAR-2[4].....	454 g E	14 g	0	16 g	0	20	79.9	.64	0
HAR-3[4].....	454 g E	14 g	0	48 g	0	60	95.3	.43	0
HAR-4[4].....	454 g E	14 g	0	80 g	0	100	96.2	.40	0

[1]Letters designate the cement copper that was being smelted.

[2]Value includes copper that was contained in the copper-bearing slag. Copper recovered = 100 pct from cement + 35 pct contained in copper-bearing slag.

[3]20 lb of copper-bearing slag were discounted; slag - 20 lb/metal = 0.29.

[4]Simulated smelting tests.

NOTE.--W- prefix indicates tests performed in the 50-kva furnace; HAR- prefix indicates tests done in a muffle furnace.

Copper-bearing slag additions of 1.1 and 20.0 pounds were substituted for silica sand in smelting tests W-6 and W-7, respectively. The recoveries from test W-6 indicated that copper-bearing slag can be used as a flux addition without adversely affecting the smelting process. Smelting test W-7 indicated that the process was not hindered by a deep slag cover which was added to improve power utilization; as shown in table 2, 35 pct of the copper contained in the copper-bearing slag was recovered as metal.

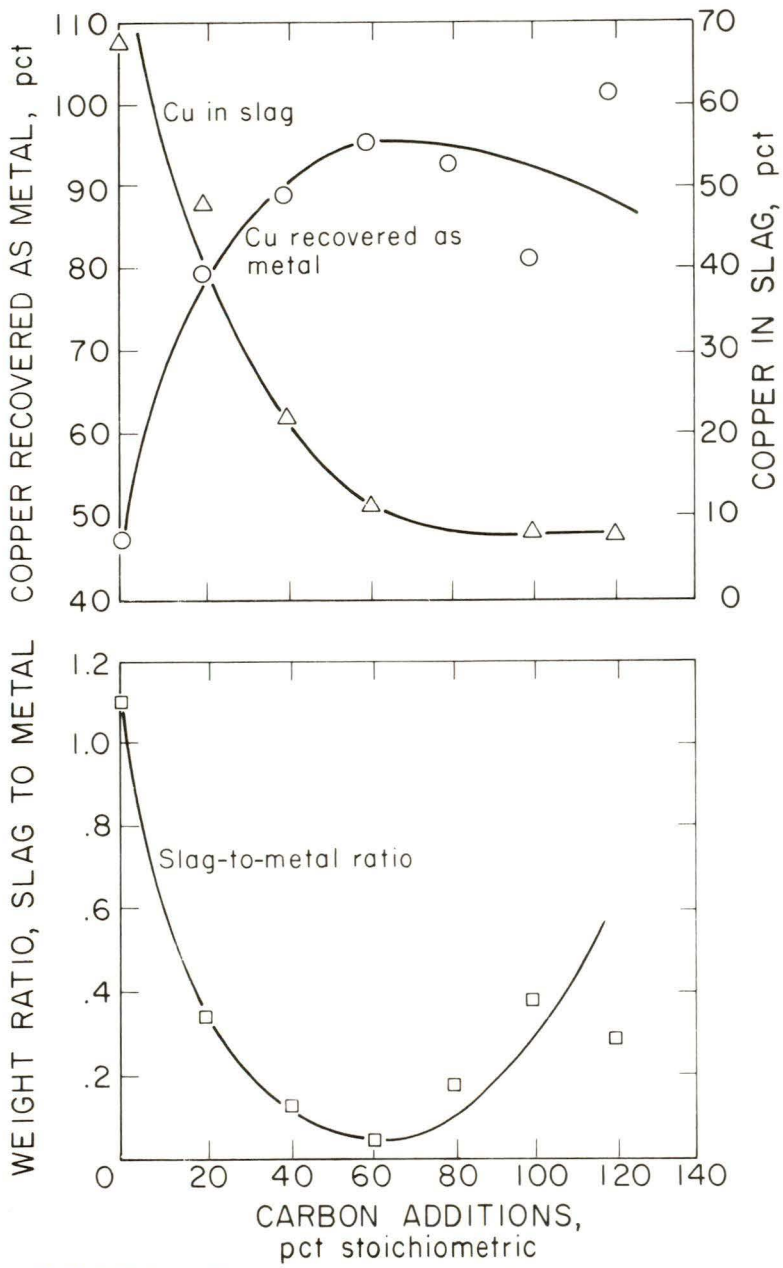

FIGURE 2. - Product distributions after 50-kva electric-arc furnace smelting tests.

Although all of the smelting products were analyzed for their principal components, more extensive analyses were made when the best recoveries were realized. The product analyses are shown in table 3. Data from tests on cement copper A were extensively evaluated to establish the slag-to-metal ratios, the copper content of slags, and the metallic copper recoveries as functions of the carbon additions. The relationships are plotted in figure 2. A slag-to-metal ratio of 0.04 and recovery of 95.2 pct of the contained copper as metal indicated that the best smelting conditions were achieved when 60 pct of the stoichiometric requirement was added to the furnace charge. Copper in the furnace slags tended to level off as the carbon additions were increased beyond 60 pct of the stoichiometric requirement. Excessive foaming, principally due to increasing slag viscosities, was observed when over 80 pct of the stoichiometric carbon requirement was added to the furnace charge. The degenerated bath conditions are reflected by the spread of data at the higher carbon levels.

TABLE 3. - Chemical analyses of smelting products from the 50-kva electric-arc furnace

Test	Stoich	Metal, pct							Slag, pct										Dust, pct		
	C, pct	Cu	Fe	O_2	Pb	Sn	C	S	Cu	Fe	Pb	Sn	S	SiO_2	Al_2O_3	CaO	MgO	C	Cu	Fe	S
W-1	0	97.9	0.32	1.74	<0.05	<0.05	ND	0	41.6	8.27	0.23	0.48	0.006	ND	ND	ND	ND	ND	58.4	5.6	3.28
W-2	0	98.8	.03	1.19	<.05	<.05	ND	0	68.2	6.78	<.05	.36	.01	ND	ND	ND	ND	ND	ND	ND	.66
W-3A	120	98.7	1.0	.01	ND	ND	ND	.249	8.0	3.6	.02	ND	.036	ND	ND	ND	ND	ND	68.0	5.0	ND
W-3B	40	99.4	<.1	.50	ND	ND	ND	.015	22.0	20.7	.18	ND	.017	ND	ND	ND	ND	ND	74.0	4.7	ND
W-4A	60	99.6	.17	.044	<.05	<.05	0.071	.014	11.2	33.9	.21	ND	.039	ND	ND	ND	ND	ND	74.0	4.0	.78
W-4B	100	97.9	3.0	.017	ND	ND	ND	.282	8.62	21.0	.04	ND	.047	ND	ND	ND	ND	ND	74.0	4.0	.57
W-5A	20	98.2	.47	1.33	ND	.03	.027	.029	48.3	14.04	ND	ND	.02	ND	ND	ND	ND	ND	73.0	5.4	.82
W-5B	80	98.7	1.17	.037	ND	.35	.186	.354	7.9	16.03	ND	ND	.02	ND	ND	ND	ND	ND	76.3	5.2	.59
W-6	60	99.7	.002	.287	ND	ND	.039	.032	16.1	5.3	ND	ND	.11	19.0	20.4	2.25	3.04	ND	66.1	5.7	ND
W-7	60	95.1	2.0	.021	ND	ND	<.001	.55	2.4	24.6	ND	ND	ND	27.0	ND	ND	ND	ND	69.5	5.2	ND
W-8	60	94.4	4.5	.007	.55	ND	.2	.33	5.6	13.2	ND	ND	.135	31.3	12.8	1.50	2.90	ND	57.0	4.8	1.41
W-9	60	90.7	9.4	.047	ND	ND	.19	.27	25.6	11.7	ND	ND	.43	ND	ND	ND	ND	5.77	ND	ND	ND
W-10	60	96.3	3.02	.012	.26	.38	.011	.21	8.14	7.45	.32	ND	.33	ND	ND	ND	ND	.125	ND	ND	ND
W-11	40	99.7	.4	.184	ND	ND	.007	.008	15.3	18.5	ND	ND	.029	ND	ND	ND	ND	.225	ND	ND	ND
W-12	80	93.0	7.0	.007	ND	ND	.016	.129	8.77	18.7	ND	ND	.156	ND	ND	ND	ND	ND	ND	ND	ND
W-13	60	90.4	7.1	.021	.09	.32	.025	.84	17.8	11.3	ND	ND	.35	ND	ND	ND	ND	ND	ND	ND	ND
W-14	80	95.4	3.7	.003	.14	.37	.009	.59	10.6	8.6	ND	ND	.33	ND	ND	ND	ND	ND	ND	ND	ND
W-15	60	92.1	6.1	ND	ND	ND	ND	ND	9.51	9.88	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
W-16	20	99.6	.4	ND	.03	ND	ND	ND	20.7	25.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
W-17	100	94.7	3.1	ND	ND	ND	ND	ND	33.8	18.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-1	40	98.1	1.1	ND	ND	ND	ND	ND	3.31	27.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-2	20	94.6	3.2	ND	ND	ND	ND	ND	19.7	22.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-3	60	98.3	.4	ND	ND	ND	ND	ND	19.6	22.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-4	100	93.9	4.0	ND	ND	ND	ND	ND	31.4	15.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND--Not determined.

NOTE.--W- prefix indicates tests performed in the 50-kva furnace; HAR- prefix indicates tests done in a muffle furnace.

The actual recoveries realized in the 50-kva furnace reflect dust losses that can be substantially decreased in a developed operation. Past experience has shown that dust losses are appreciably less in a larger system and that recycling techniques can further lower the net loss to a negligible level. By approximating the weight losses from gaseous evolution of the reaction products and accounting for them in a material balance, the dust losses in the laboratory-scale tests on cement copper were calculated as shown in table 4. Assuming minimal dust losses, the following relationship becomes valid:

Copper input - copper lost in slag = copper recovery.

Copper recoveries for all of the laboratory-scale smelting tests were calculated from the actual copper contents of the slags as shown in table 5 and plotted in figures 3, 4, and 5.

TABLE 4. - Material balances for laboratory-scale smelting tests on cement copper

Test	Input, lb	Expected weight loss, lb				Corrected input, lb	Products, lb	Solids recovered, pct
		O_2	C	H_2O	Total			
W-2.....	36.5	3.71	0	1.33	5.04	31.5	25.3	80.4
W-3A.....	40.7	3.71	3.33	1.30	8.34	32.4	33.5	103.5
W-3B.....	37.1	3.71	1.11	1.38	6.20	30.9	25.5	82.5
W-4A.....	38.3	3.71	1.67	1.04	6.42	31.9	25.3	[1] 79.4
W-4B.....	40.2	3.71	2.78	2.27	8.76	31.4	30.0	95.4
W-5A.....	36.8	3.71	.56	1.50	5.77	31.0	26.7	86.0
W-5B.....	38.6	3.71	2.22	1.43	7.36	31.2	27.6	88.3
W-6[2].....	53.7	5.22	3.91	.03	9.16	44.5	40.3	90.5
W-7[2].....	68.3	4.53	3.39	2.06	9.98	58.3	62.6	107.3
Average	-	-	-	-	[3] 9.7	-	-	[4] 90.3

[1] Some unweighed residue was raked from the furnace before starting charge B.
[2] Values do not include copper-bearing slag.
[3] Average dust loss, in percent.
[4] Average corrected solids recovery, in percent.

NOTE.--W- prefix indicates tests performed in the 50-kva furnace.

TABLE 5. - Adjusted copper recoveries from smelting tests in the 50-kva electric-arc furnace

Test	Cement copper	Copper charged, lb	Carbon added, pct stoich	Copper lost in slag, lb	Copper recovered[1] as metal, pct
W-2.....	A	25.1	0	9.03	64.02
W-3A.....	A	25.2	120	.60	97.61
W-3B.....	A	25.2	40	.66	97.40
W-4A.....	A	25.4	60	.11	99.56
W-4B.....	A	25.2	100	2.44	90.3
W-5A.....	A	25.0	80	3.23	87.08
W-5B.....	A	25.0	60	.32	98.72
W-6A[2].....	A	36.7	60	.76	97.92
W-7[3].....	A	33.3	60	.70	[4]97.90
W-8.....	B	25.1	60	.39	98.5
W-9.....	D	28.5	60	.21	99.3
W-10.....	D	28.9	60	.07	99.8
W-11.....	D	28.9	40	1.60	94.5
W-12.....	D	28.9	80	.19	99.3
W-13.....	E	18.8	60	1.12	94.0
W-14.....	E	18.8	80	.43	97.7
W-15.....	E	15.6	60	.55	96.5
W-16.....	D	24.8	20	.79	96.8
W-17.....	D	24.8	100	.74	97.0
HAR-1[5]....	E	284 g	40	ND	[6]96.1
HAR-2[5]....	E	284 g	20	ND	[6]79.9
HAR-3[5]....	E	284 g	60	ND	[6]95.3
HAR-4[5]....	E	284 g	100	ND	[6]96.2

ND--Not determined.
[1]Copper input - copper lost in slag = copper recovery.
[2]1.1 lb copper-bearing furnace slag was used as flux.
[3]20 lb copper-bearing furnace slag were added to the charge.
[4]Includes copper contained in copper-bearing furnace slag.
[5]Simulated smelting tests.
[6]Recovered as metal.

NOTE.--W- prefix indicates tests performed in the 50-kva furnace; HAR- prefix indicates tests done in a muffle furnace.

The cement coppers smelted in the 50-kva electric-arc furnace contained 62.5 to 82.5 pct copper. Although the copper recovery curves that are compared in figure 6 indicated more carbon was required to maximize the metallic copper recovery from cement copper E, it was concluded that the best results would be realized in a pilot-scale program by adding 60 pct of the carbon that would be required to combine with the contained oxygen in the furnace charge.

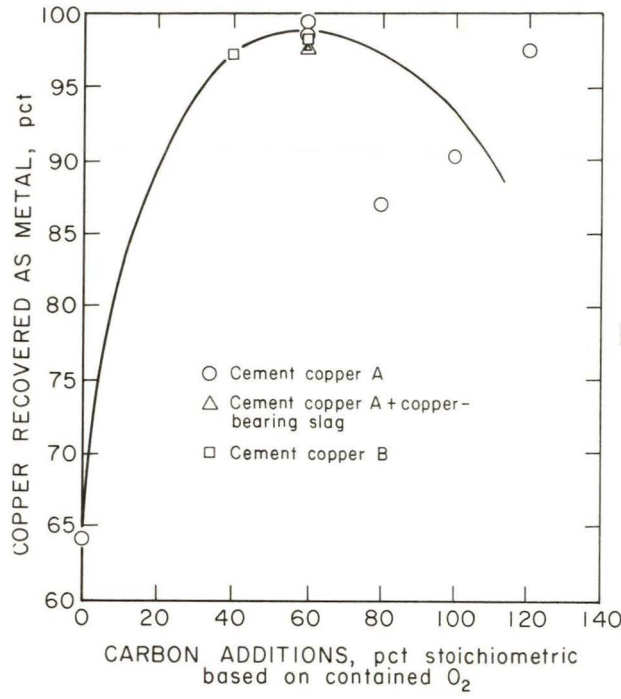

FIGURE 3. - Adjusted metallic copper recoveries from cement coppers A and B versus carbon additions.

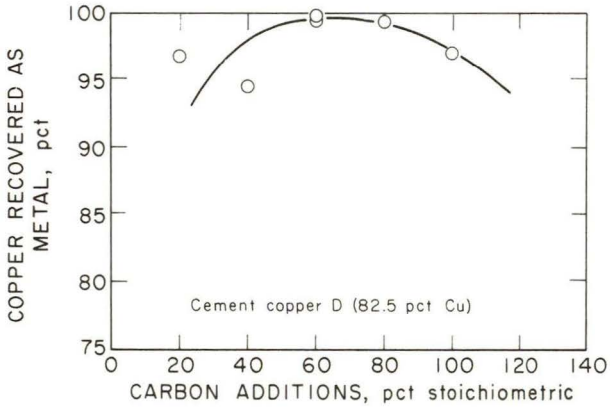

FIGURE 4. - Adjusted metallic copper recoveries from cement copper D versus carbon additions.

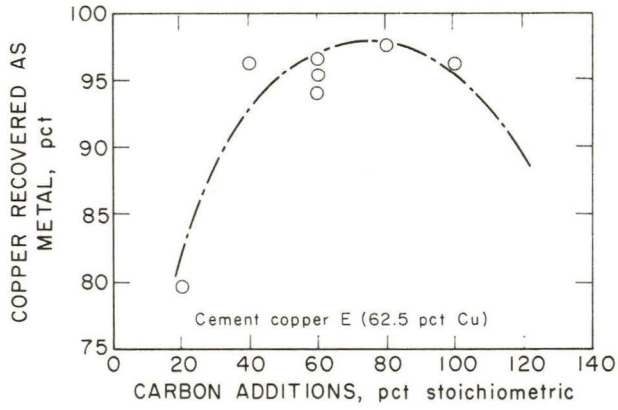

FIGURE 5. - Adjusted metallic copper recoveries from cement copper E versus carbon additions.

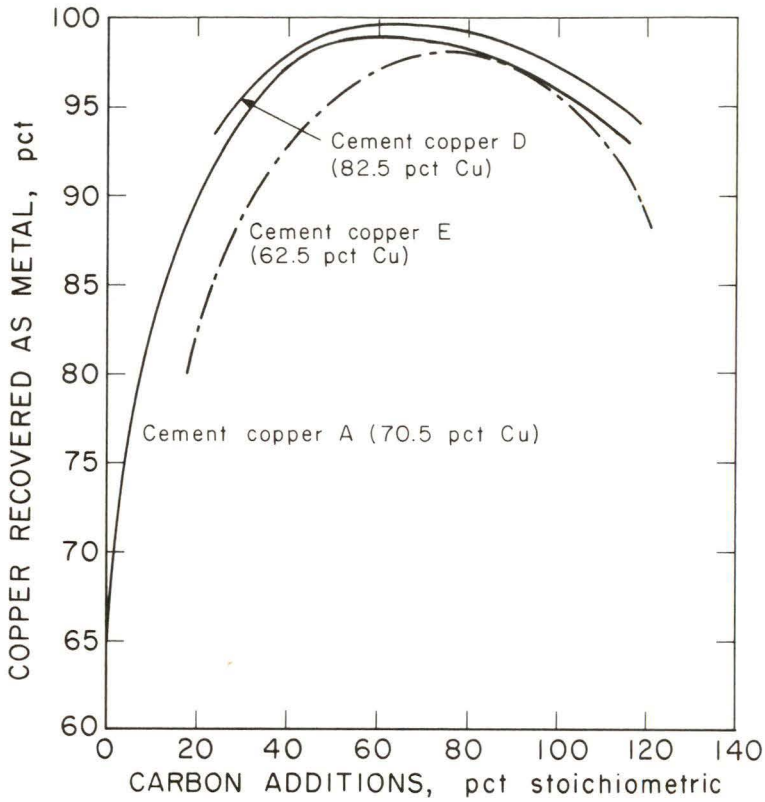

FIGURE 6. - Comparison of the adjusted metallic copper recoveries from the cement coppers that were smelted in the 50-kva electric-arc furnace.

Smelting Tests in the 800-kva Electric-Arc Furnace

Operating parameters established during the laboratory-scale smelting tests were used successfully in the pilot-scale smelting tests. The pilot-scale smelting program was designed to establish materials and energy requirements for a continuous system at a representative smelting rate.

Materials Used for Smelting Tests in the 800-kva Electric-Arc Furnace

A total of 20 tons of cement copper C (table 1) was smelted during 12 tests in the 800-kva furnace. Silica sand and pebble lime were added to provide a synthetic slag and to flux the small amount of gangue in the cement copper. Petroleum coke was used in all but one test; in the exception, shell carbon was used to compare the carbon efficiencies.

The charge materials were blended in the 8-inch-diameter zigzag blender shown in figure 7 by proportioning the blend components into the hopper of a 4-inch bucket elevator that lifted feed into the blender. The blended material was discharged into 55-gal drums. The entire unit was connected to a 7,500-cu-ft/min dust collection system with dampers adjusted to prevent removing fines from the materials as they were being blended.

Equipment and Operating Procedures for Smelting Tests in the 800-kva Electric-Arc Furnace

Figure 8 shows the 800-kva electric-arc furnace that was used for this investigation. The three 4-inch-diameter electrodes were positioned in a conventional "delta" configuration on 12-inch centers. The cylindrical furnace shell wall was lined with magnesite bricks, and the furnace hearth was sloped with alumina ram mix. The hearth area was 6.7 sq ft, and the normal depth of the bath was 20 inches.

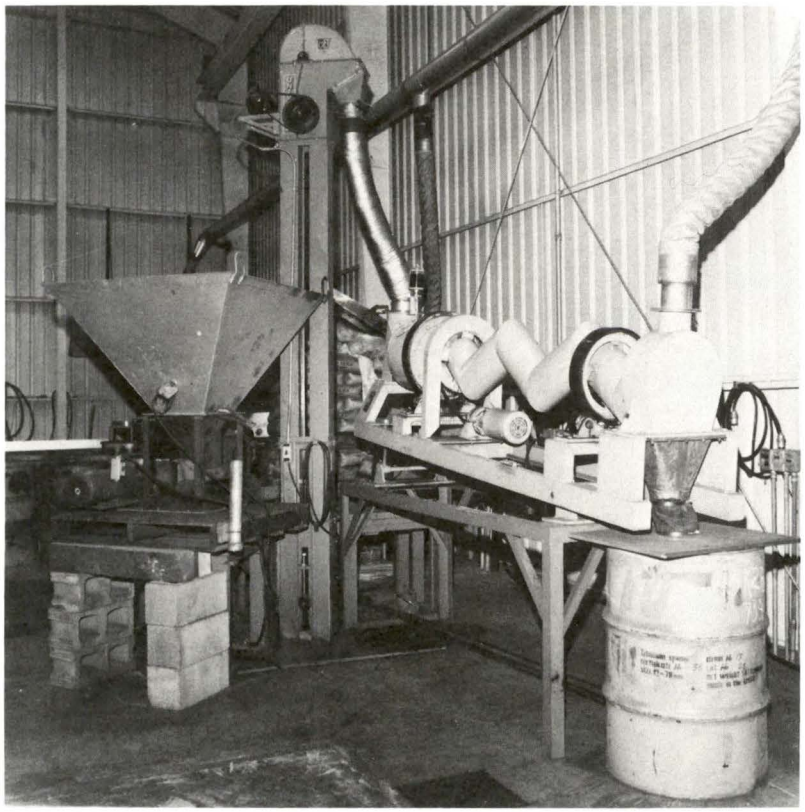

FIGURE 7. - 8-inch-diameter zigzag blender.

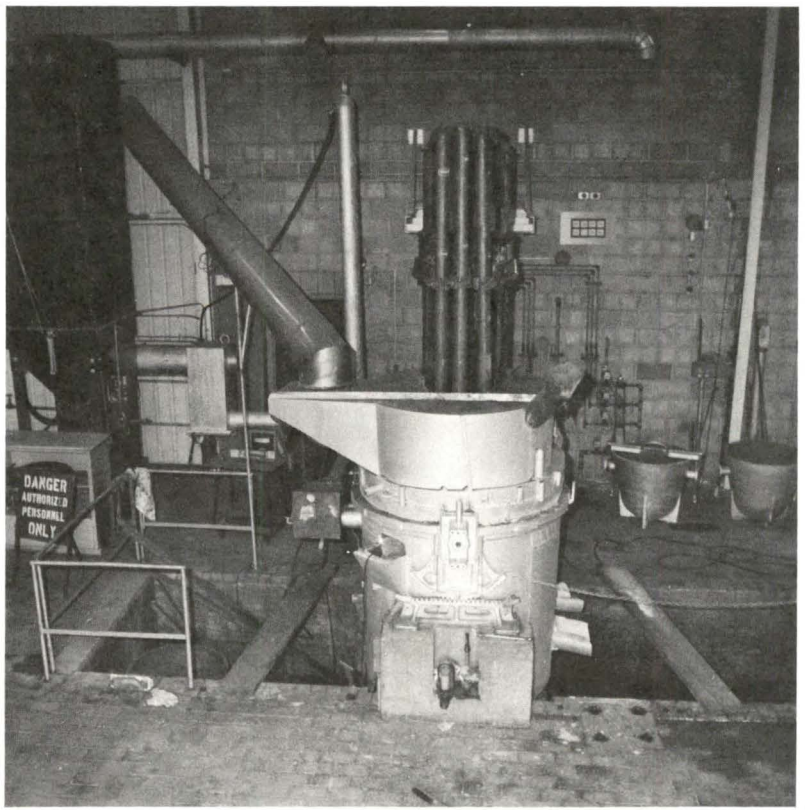

FIGURE 8. - 800-kva electric-arc furnace.

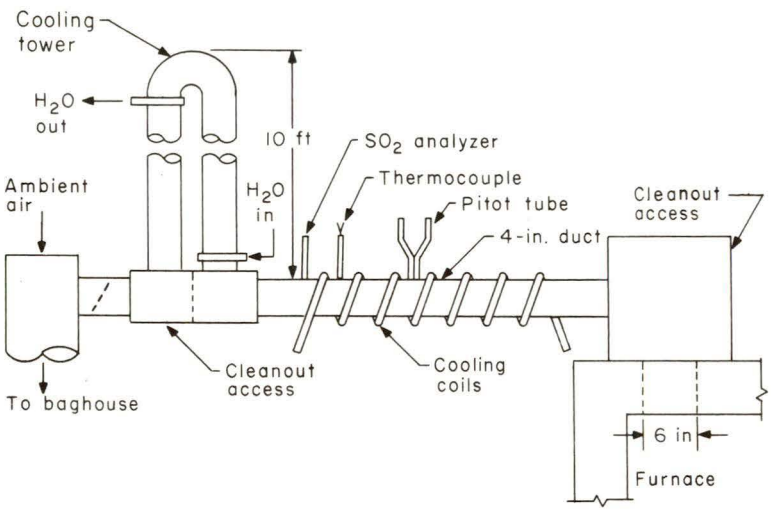

FIGURE 9. - Offgas system for 800-kva electric-arc furnace.

The charge material was gravity-fed through the furnace roof, and feed rates were controlled with a 4-inch-wide variable-speed belt feeder. A stainless steel feed chute that extended inside the furnace from roofline halfway to the furnace hearth was installed to protect the feed material from the smelting atmosphere.

The small baghouse to the left of the furnace in figure 8 quantitatively collected the entrained dusts from the furnace offgases. The baghouse was connected to the furnace by the offgas train shown in figure 9. The offgas-monitoring train was equipped with an infrared gas analyzer to continuously monitor SO_2 levels. The small baghouse and plenum hood were evacuated by a 7,500-cu-ft/min fan that exhausted into a positive-pressure cyclone and baghouse system. Sulfur dioxide was removed from the dust-free offgases in a countercurrent scrubber in which sodium carbonate solution percolated down through a packaged bed.

Metal products from the smelting tests were poured into 50-pound pig molds, and the slags were cooled in conical ladles large enough to contain all of the slag poured during each tap. All of the slag was crushed in a primary jaw crusher and gyratory mill before the material was split down for final processing. The slag samples were ground to minus 80 mesh and thoroughly blended before they were submitted for chemical analyses. Random drill samples were taken from each of the metal pigs, and a composite sample was prepared from each tap for chemical analyses. A computer-controlled direct-reading optical spectrograph became available for the last six smelting runs. The spectrograph permitted determinations of iron in copper metal while the last six smelting runs were in progress. The sampling and analytical procedures regarding this portion of the work are described in the appendix.

Results of Smelting Tests in the 800-kva Electric-Arc Furnace

Twelve pilot-scale smelting tests were made using a range of charge compositions and operating parameters to improve the quantity and quality of the copper metal product. The charge compositions and product analyses are shown in table 6. Sequential additions of 40 and 80 pct of the stoichiometric carbon requirement were added to the furnace for test LMC-3 in lieu of the 60-pct stoichiometric carbon additions that were used for the rest of the tests. Variables that were expected to affect the reductant behavior were also introduced in tests LMC-4 and LMC-5; in these tests, shell carbon was used in lieu of petroleum coke, and the blended furnace charge was pelletized, respectively.

TABLE 6. - Materials data from smelting tests in the 800-kva electric-arc furnace

Test	Charge composition						Metal									Slag												
	Cement, lb	Petroleum coke, lb	Stoich C, pct	SiO_2, lb	CaO, lb	Cu, lb	Taps	Wt, lb	Analysis, pct							Taps	Wt, lb	Analysis, pct										
									Cu	Fe	Pb	Zn	O_2	S	C			Cu	Fe	Pb	Zn	O_2	S	C	SiO_2	Al_2O_3	CaO	MgO
LMC-1..	3,091	281	60	192	-	30	1....	1,463	98.6	1.26	0.10	0.04	0.021	0.58	0.002	1.....	79	9.10	36.3	NA	NA	NA	0.45	NA	NA	NA	NA	NA
							2....	604	95.3	4.60	.11	.05	.025	.66	.002	2.....	220	5.66	31.7	NA	NA	NA	.35	NA	NA	NA	NA	NA
																Flue dust[1]	168	37.5	6.8	2.34	1.44	15.3	5.0	3.37	NA	NA	NA	NA
LMC-2..	3,045	273	60	246	153	40	1....	1,245	94.2	4.97	.11	.06	.022	.66	.003	1.....	162	4.37	25.8	NA	NA	NA	.12	NA	35.3	5.78	16.0	1.36
							2....	958	95.1	4.02	.11	.05	.011	.68	.002	2.....	636	2.11	24.1	NA	NA	NA	.14	NA	38.2	6.71	15.0	2.03
																Flue dust[1]	60	40.4	9.1	1.68	2.73	19.8	5.85	.62	NA	NA	NA	NA
LMC-3..	2,985	269	{[2]40 80}	244	153	35	1....	991	98.9	.65	ND	ND	.051	.43	.002	1.....	221	5.13	29.9	NA	NA	NA	.033	.11	NA	NA	NA	NA
							2....	908	95.2	4.24	ND	ND	.026	.58	.003	2.....	429	3.10	27.3	NA	NA	NA	.11	.24	NA	NA	NA	NA
																Flue dust[1]	108	50.5	11.9	NA	NA	23.6	5.07	.48	NA	NA	NA	NA
LMC-4..	3,505	[3]285	60	275	153	30	1....	1,402	98.8	1.20	ND	ND	.012	.35	.001	1.....	102	15.5	28.3	NA	NA	NA	.22	.20	NA	NA	NA	NA
							2....	949	97.5	2.06	ND	ND	.042	.41	.004	2.....	821	1.68	29.8	NA	NA	NA	.13	.056	NA	NA	NA	NA
																Flue dust[1]	168	49.4	8.18	NA	NA	25.6	3.58	2.75	NA	NA	NA	NA
LMC-5[4].	2,814	252	60	232	153	31	1....	1,169	99.0	.46	ND	ND	.019	.50	.002	1.....	138	3.66	27.1	NA	NA	NA	.087	.077	32.5	4.30	16.8	NA
							2....	774	97.4	1.97	ND	ND	.023	.58	.004	2.....	559	1.43	25.8	NA	NA	NA	.131	.158	38.2	5.34	13.2	NA
																Flue dust[1]	68	34.1	10.6	NA	NA	21.1	4.66	2.99	NA	NA	NA	NA
LMC-6..	2,446	219	60	150	[5]600	30	1....	900	99.4	.12	ND	ND	.028	.41	.002	1.....	177	3.90	34.6	NA	NA	NA	.047	.092	30.5	8.88	7.69	NA
							2....	761	97.8	1.77	ND	ND	.009	.45	.005	2.....	729	2.09	34.1	NA	NA	NA	.156	.109	34.4	8.64	6.76	NA
																Flue dust[1]	76	39.0	7.29	NA	NA	20.8	5.11	.48	NA	NA	NA	NA
LMC-7..	2,995	270	60	157	[6]200	30	1....	981	96.3	3.1	.16	.11	.013	.72	.001	Slag[7].....	684	3.0	34.3	.03	.07	NA	NA	NA	36.1	6.48	.84	2.56
							2....	509	97.3	2.7	.14	.10	.020	.76	.002	Flue dust[1]	105	39.0	6.20	1.75	4.0	NA	NA	NA	NA	NA	NA	NA
							3....	474	96.1	3.8	.11	.05	.017	.77	.002														
							4....	113	85.3	13.6	.10	.08	.019	.82	.076														
LMC-8..	3,007	266	60	243	153	30	1....	662	98.4	1.06	.07	.03	.009	.43	.002	Slag[7].....	497	3.61	32.7	.02	.07	NA	NA	NA	NA	NA	NA	NA
							2....	552	97.5	1.40	.09	.04	.009	.46	.001	Flue dust[1]	92	51.2	10.3	NA	NA	17.9	1.77	1.77	NA	NA	NA	NA
							3....	372	98.1	1.29	.09	.03	.006	.43	.001														
							4....	306	96.5	2.52	.10	.07	.011	.57	.002														
LMC-9..	2,810	253	60	234	153	25	1....	738	97.6	2.52	.11	.05	.017	.54	.002	Slag[7].....	665	1.44	27.4	.01	.03	NA	NA	NA	NA	NA	NA	NA
							2....	437	98.5	1.37	.11	.06	.016	.54	.001	Flue dust[1]	74	52.0	10.6	NA	NA	19.1	1.85	2.40	NA	NA	NA	NA
							3....	648	97.3	2.68	.09	.07	.009	.55	.001														
LMC-10.	2,967	266	60	245	153	20	1....	746	98.3	1.7	.09	.04	.011	.45	<.001	Slag[7].....	693	1.89	31.6	.02	.07	NA	NA	NA	32.3	NA	NA	NA
							2....	489	98.3	1.7	.09	.05	.017	.48	.001	Flue dust[1]	82	53.3	10.1	.47	.96	17.8	1.85	1.38	NA	NA	NA	NA
							3....	460	97.4	2.1	.11	.05	.021	.54	.001														
							4....	150	97.8	2.2	.13	.06	.018	.62	.001														
LMC-11.	2,647	237	60	265	153	25	1....	542	96.4	.64	.10	.03	.044	.53	.004	Slag[7].....	661	2.72	30.1	.04	.10	NA	NA	NA	35.9	NA	NA	NA
							2....	882	95.5	1.48	.13	.05	.018	.60	.001	Flue dust[1]	93	37.0	10.0	NA	NA	NA	NA	NA	NA	NA	NA	NA
LMC-12.	2,426	224	60	254	153	38	1....	584	94.1	2.7	.28	.16	.023	.74	.002	Slag[7].....	969	.90	21.6	.01	.06	NA	NA	NA	39.3	NA	NA	NA
							2....	2,602	93.1	4.3	.39	.14	.014	.78	.002	Flue dust[1]	53	45.4	10.7	NA	NA	NA	NA	NA	NA	NA	NA	NA

NA--No analysis. ND--Not detected.
[1]Dust in small baghouse plus accretions in the 4-inch offgas duct.
[2]40 percent of the stoichiometric carbon requirement was included before metal tap 1.
[3]Shell carbon.
[4]Pelletized furnace charge.
[5]400 lb of slag from test LMC-3 (No. 2) and 200 lb of slag from test LMC-4 (No. 2).
[6]Reverberatory furnace slag.
[7]Composite.

NOTE.--LMC- prefix indicates tests done in the 800-kva furnace.

The changes in operating parameters made for each test and the resulting smelting conditions are shown in table 7. Approximately 65 pct of each offgas volume listed in the table was due to ambient air flowing through the system. When more carbon was added to the furnace charge during test LMC-3, the SO_2 level decreased in the offgas stream. The decrease was attributed to additional carbon causing a more reducing atmosphere over the molten bath.

TABLE 7. - Operating data from smelting tests in the 800-kva electric-arc furnace

Data	Test LMC-					
	1	2	3	4	5	6
Smelting rate.....lb/hr..	[1] 1,500 [2] 862	955	972	1,054	1,100	1,117
Power consumption.....kwhr/ton..	495	493	422	389	490	379
Mean bath temperature.....° C..	[1] 1,245 [2] 1,309	1,351	1,362	1,349	1,285	1,343
Offgas volume.....scfm..	132	94	[3] 90 [4] 84	110	97	100
Average offgas temperature.....° C..	730	769	688	615	718	NA
Average SO_2 content of offgas..pct..	0.21	0.6	[3] 0.83 [4] 0.24	0.45	0.26	NA
Electrode consumption.....lb/ton..	17.3	10.1	22.8	8.9	15.3	20.4
	7	8	9	10	11	12
Smelting rate.....lb/hr..	951	946	738	826	778	675
Power consumption.....kwhr/ton..	521	313	434	405	452	NA
Mean bath temperature.....° C..	1,301	1,238	1,233	1,206	1,222	[5] 1,280
Offgas volume.....scfm..	96	100	117	92	106	96
Average offgas temperature.....° C..	726	608	429	626	560	720
Average SO content of offgas..pct..	1.2	NA	0.49	0.35	NA	NA
Electrode consumption.....lb/ton..	21.4	12.4	22.4	NA	19.8	47

NA--Not available.
[1] During the first 2/3 of the test.
[2] During the last 1/3 of the test.
[3] When the furnace charge contained 40 pct of the stoichiometric carbon requirement.
[4] When the furnace charge contained 80 pct of the stoichiometric carbon requirement.
[5] Final bath temperature was 1,395° C.

Using chemical analyses of the furnace charges and smelting products, copper and iron accountabilities were calculated for each test as shown in table 8. Accountabilities exceeding 100 pct can be attributed to varying furnace bath temperatures causing material carryover from one test to another. An exceptionally low iron accountability resulted from the new furnace lining adsorbing approximately one-half of the slag during test LMC-1. The materials carryover was particularly high from test LMC-11 to LMC-12, when extremely low and high furnace bath temperatures were maintained to study the effect on iron distribution.

TABLE 8. - Accountability of copper and iron during the pilot-scale smelting tests

Test	Distribution and accountability, pct				Total accounted for, pct
	Metal	Slag	Baghouse[1]	Miscellaneous[2]	
LMC-1:					
Copper	91.4	0.9	3.2	0.1	95.6
Iron	15.3	32.7	4.5	3.6	56.1
LMC-2:					
Copper	95.2	.9	1.7	1.0	98.9
Iron	33.7	65.7	3.4	3.7	[3]106.4
LMC-3:					
Copper	86.2	1.1	2.5	3.8	93.6
Iron	16.6	67.6	3.9	2.9	91.0
LMC-4:					
Copper	92.4	1.2	3.7	4.2	[3]101.5
Iron	10.6	80.0	4.6	4.0	99.2
LMC-5:					
Copper	94.8	.6	4.6	2.0	[3]102.0
Iron	7.5	54.0	9.5	11.4	82.4
LMC-6:					
Copper	92.6	1.2	1.7	5.9	[3]101.4
Iron	3.6	76.1	1.5	13.5	94.7
LMC-7:					
Copper	93.0	1.0	3.4	1.6	99.0
Iron	22.0	66.1	3.8	1.4	93.3
LMC-8:					
Copper	86.5	.8	3.2	6.8	97.3
Iron	5.4	54.9	5.1	13.9	79.3
LMC-9:					
Copper	88.8	.5	2.6	8.9	100.8
Iron	15.3	77.9	4.0	9.1	[3]106.3
LMC-10:					
Copper	85.7	.6	3.1	9.5	98.9
Iron	11.8	75.8	4.4	9.6	[3]101.6
LMC-11:					
Copper	72.1	1.0	2.9	NA	[4]76.0
Iron	6.4	77.1	5.0	NA	[4]88.5
LMC-12:					
Copper	170.0	.5	3.1	NA	[4]173.6
Iron	53.9	88.3	4.5	NA	[4]146.7

NA--Not available.

[1] Includes flue dust and feed material entrained in the plenum hood.

[2] Includes spilled materials and accretions removed from the furnace after a test.

[3] Varying furnace bath temperatures caused material carryover from one test to another.

[4] The low operating temperatures that were maintained in test LMC-11 caused a lot of material to be carried over to test LMC-12.

NOTE.--LMC- prefix indicates tests done in the 800-kva furnace.

The copper recoveries and distributions that resulted from the pilot-scale smelting tests reflect dust losses and amounts of unreacted residues that would not be realized in a commercial system that was operating continuously. To project the metallic copper recoveries that can be realistically expected from the carbothermic reduction of cement copper in a commercial operation, the data from each pilot-scale test were treated as shown in table 9. The results of the calculations are shown in table 10.

TABLE 9. - Copper recovery calculated for a continuous operation (test LMC-5)

Copper input, lb:	
Copper in cement copper	1,983
Copper starting block	31
Total	2,014
Copper recovery, lb:	
Copper metal	1,915
Copper in slag	13
Copper in small baghouse and 4-inch cleanout	23
Copper in large baghouse	66
Copper in furnace residue	41
Total	2,058
Calculated copper metal recovery, pct:	
Copper recovered as metal	95.1
Copper in unreacted materials	[1] 5.3
Total	100.4

[1] Includes cement copper that was collected through the plenum hood into the large baghouse and furnace residue that was collected after the test had been completed.

TABLE 10. - Continuous copper recoveries as calculated from the pilot-scale smelting test results

Test	Continuous copper recovery (pct of Cu in furnace charge)
LMC-1	91.1
LMC-2	98.5
LMC-3	86.6
LMC-4	96.8
LMC-5	100.0
LMC-6	94.2
LMC-7	97.9
LMC-8	94.0
LMC-9	101.4
LMC-10	96.0
LMC-11	NA
LMC-12	NA

NA--Not available.

NOTE.--LMC- prefix indicates tests done in the 800-kva furnace.

DISCUSSION

Copper recoveries ranged from 85.7 to 100.6 pct over the pilot-scale test series. Several alterations were made in the charge compositions established by the laboratory-scale tests; each alteration had either a deleterious or no appreciable effect on the copper recovery. Lowering the carbon addition to 40 pct of the stoichiometric requirement during the first half of test LMC-3 increased the SO_2 level in the furnace offgases. The equivalent sulfur elimination was exceptionally low when the carbon addition was increased to 80 pct of the stoichiometric requirement during the last half of the test. However, cycling the carbon addition did not affect the composition of the metallic copper products or the amount of copper that was recovered as metal. When the slag burden was increased substantially for test LMC-6, the calculated copper recovery for a continuous operation was lowered because the copper concentrations of the slag remained about the same as when the slag-to-metal ratio was much less in the rest of the smelting tests.

Attempts were made to increase the carbon utilization by using shell carbon in lieu of petroleum coke and pelletizing the blended furnace charge in tests LMC-4 and LMC-5, respectively. Lower copper recoveries resulted from using shell carbon because of increased dust losses. Pelletizing the furnace charge did not affect the copper recovery.

Moisture contents of the blended furnace charges were carefully monitored during six of the pilot-scale smelting tests. Although the correlation between the moisture contents of the charge materials and copper recoveries showed some variation, it was more evident that the dust losses were appreciably lower when the moisture content of the feed was at least 1 wt-pct. Figure 10 shows that moisture contents above the 1 wt-pct level do not further decrease the dust losses sufficiently to warrant an inevitably higher energy consumption.

It was concluded that the furnace bath temperature was the dominant parameter affecting the quality of the copper metal that was being produced. Frequent bath temperature measurements and corresponding iron analyses of the metal portion of the furnace bath were plotted as shown for test LMC-9 in figure 11. Areas under the curve were divided by the elapsed time to indicate an effective bath temperature prior to each sampling, and the resulting relationships were plotted for each set of data as shown in figure 12. Although an effective bath temperature as low as 1,170° C and a corresponding iron content of 0.25 wt-pct were recorded, the highest continuous copper recoveries were calculated from tests LMC-5 and LMC-9, when the mean operating temperatures were 1,285° and 1,233° C, respectively. The copper metals that were recovered from tests LMC-5 and LMC-9 contained 1.06 and 2.30 wt-pct iron, respectively.

All of the copper contents in the tapped slags, except for test LMC-1, which was run in a new furnace lining, and the exceptionally high copper content of the first slag tap in test LMC-4, were plotted in relation to the iron concentrations of the corresponding metallic coppers, as shown in figure 13. The copper content of the furnace slag reaches a minimum when the smelting parameters produce a copper metal that contains between 2 and 2.5 wt-pct iron. The corresponding smelting temperature is approximately 1,250° C, as shown in

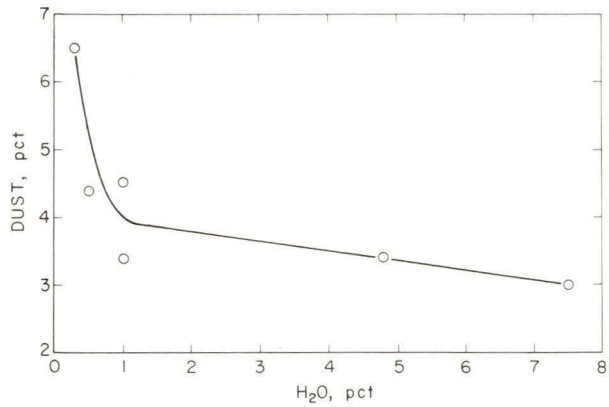

FIGURE 10. - Effect of moisture content in the furnace feed on dust losses.

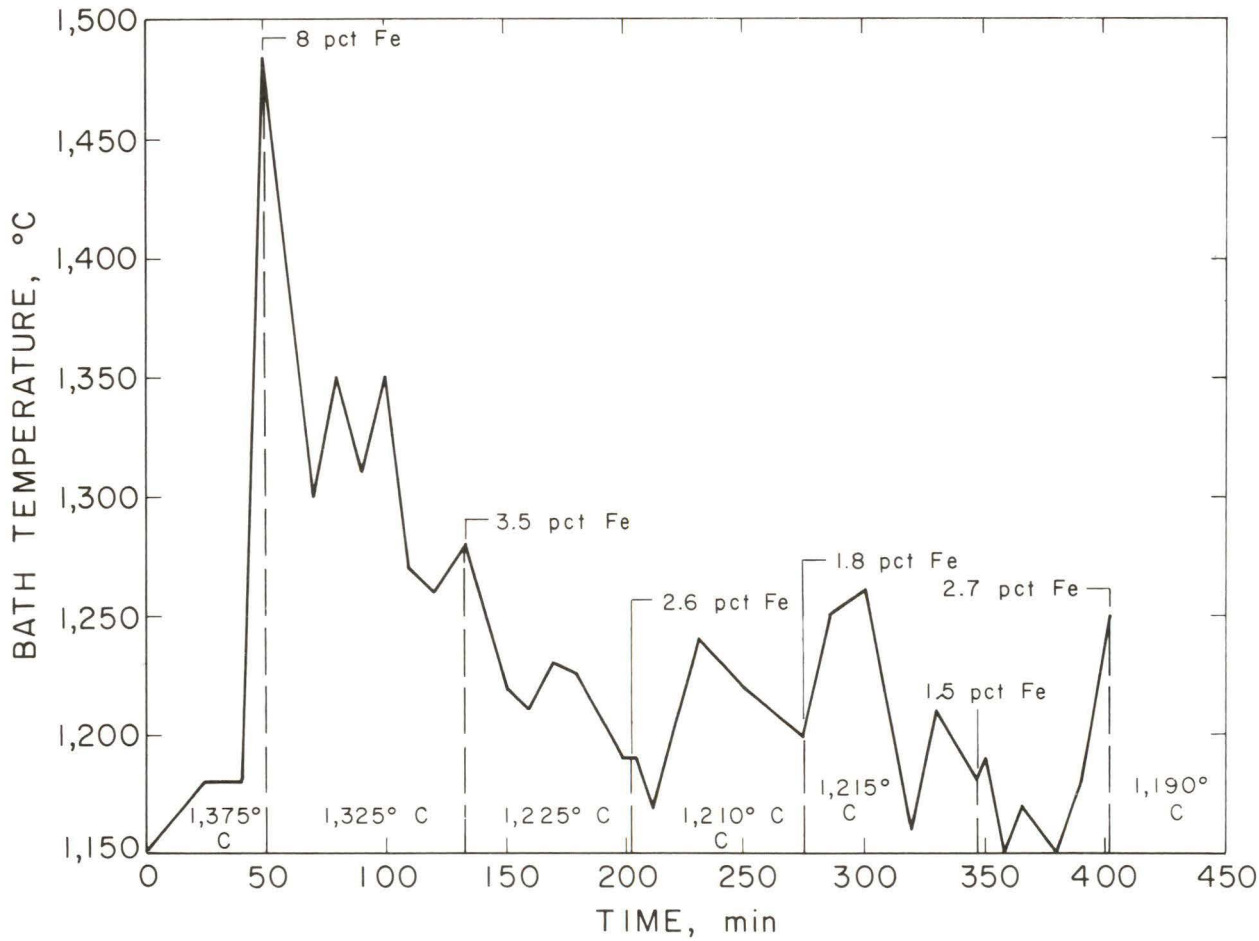

FIGURE 11. - Effect of bath temperature on the iron content of the copper metal during test LMC-9.

figure 12. Figures 12 and 13 indicate that blister-grade copper can be recovered by tapping the metal from the furnace at a temperature below 1,200° C and that low copper losses can be realized by periodically removing the minimal slag burden from the furnace at approximately 1,250° C.

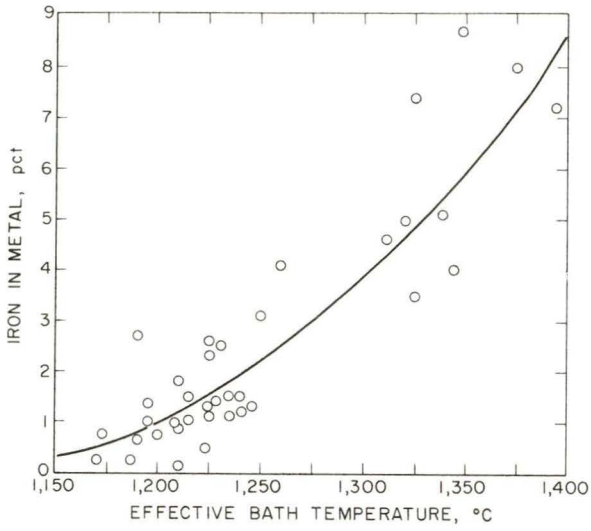

FIGURE 12. - Effect of furnace bath temperature on the iron content of the copper metal.

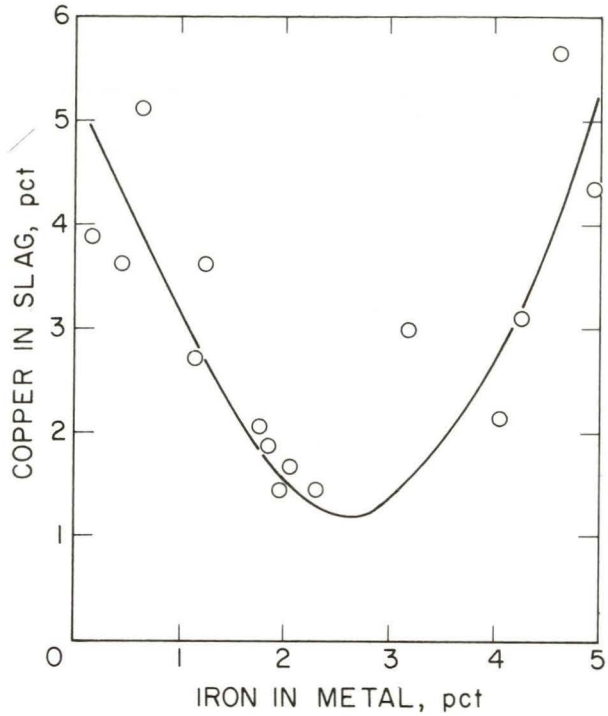

FIGURE 13. - Copper contents of the slags that were tapped during the pilot-scale smelting tests as related to the iron contents of the corresponding metals.

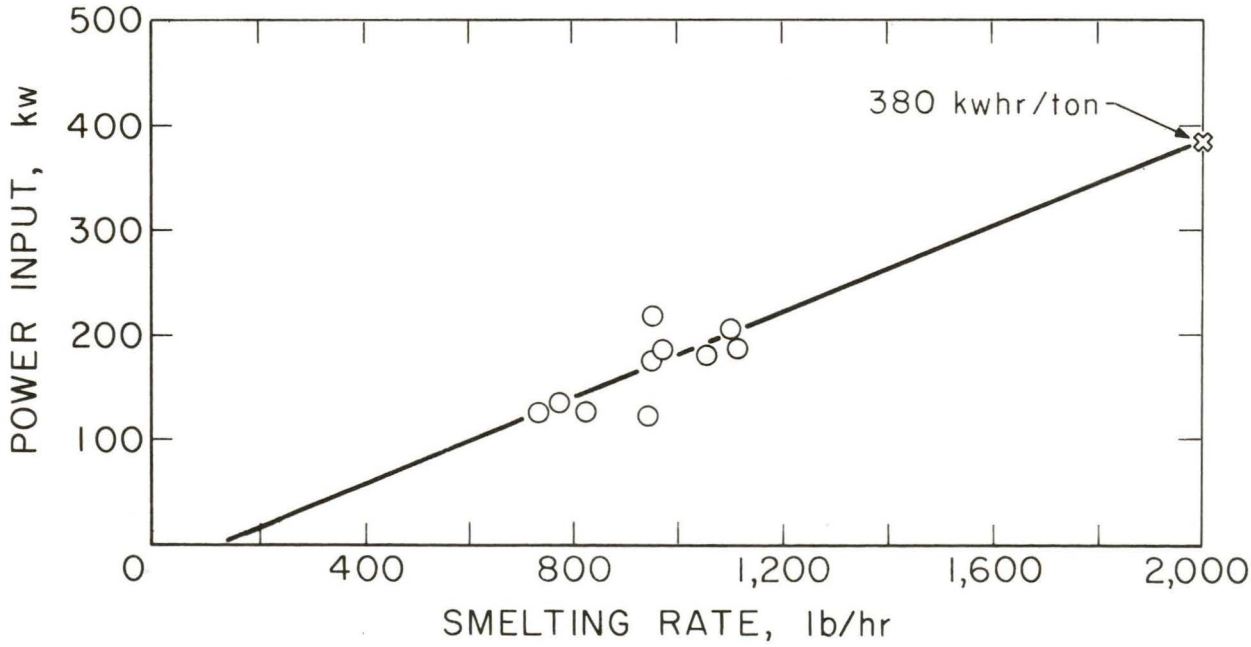

FIGURE 14. - Energy requirement for smelting cement copper.

Smelting rates ranged from 675 to 1,500 lb/hr and energy consumptions ranged from 313 to 521 kwhr/ton during the pilot-scale smelting test series. To compensate for the wide range of heat losses that occurred as the bath temperatures, smelting rates, and associated parameters were changed, the power input data were extrapolated to a nominal smelting rate of 2,000 lb/hr. The extrapolation indicates an energy requirement of 380 kwhr/ton as shown in figure 14.

CONCLUSION

A blister-grade copper can be recovered from cement coppers by carbothermic reduction in an electric-arc furnace. The reductant requirements can be based on providing 60 pct of the carbon that is required to form carbon monoxide with the contained oxygen in varied grades of cement copper. The highest copper recoveries and best metal quality can be achieved by tapping slag from the furnace at approximately 1,250° C and removing metal from the furnace at less than 1,200° C. The electric-arc-furnace smelting of cement copper requires approximately 380 kwhr/ton of cold charge.

APPENDIX.--ANALYTICAL TECHNIQUES

by

R. F. Farrell[1] and W. J. Niebuhr[2]

The determination of iron in copper was performed during the smelting cycle using the computer-controlled direct-reading spectrograph. Within 10 min of the button pour, qualitative results were obtained for concentrations up to 3 pct; semiquantitative results were obtained for concentrations above 3 pct. Quantitative results above 3 pct were later obtained by solution X-ray emission techniques.

The rapid determination of iron in copper was an important requirement in the development of a process to smelt cement copper in an electric-arc furnace. The computer-controlled direct-reading optical spectrograph was selected to perform the analysis.

This instrument, which represents a revolutionary approach in direct-reading spectroscopy, is shown in figures A-1 and A-2. It is a complete, computer-controlled spectrochemical system. The basic system can be programed to analyze up to 50 elements simultaneously in any combination. The analyst can vary the operational parameters with a terminal teletype keyboard. The computer monitors and controls the entire operation. It programs the analysis, makes all computations, and prints the record of the analyses in the desired format. As shown in figure A-3, the test sample button should be 1-1/4 inch in diameter. The excitation is essentially a surface phenomenon, with sample penetration by the electrical discharge a few thousandths of an inch deep. The excitation zone is a circle approximately 1/4 inch in diameter.

To check the accuracy of the method, sample buttons analyzed by the direct reader were analyzed by atomic absorption spectrophotometry. A comparison is shown below:

Sample	Direct reader Fe, pct	Atomic absorption Fe, pct
1.....	0.25	0.22
2.....	1.10	1.10
3.....	1.40	1.44
4.....	2.90	3.10

The percent standard deviation was determined at 0.25 and 1.35 pct iron by replicate analysis. The overall percent standard deviation was calculated to be about ±3 pct.

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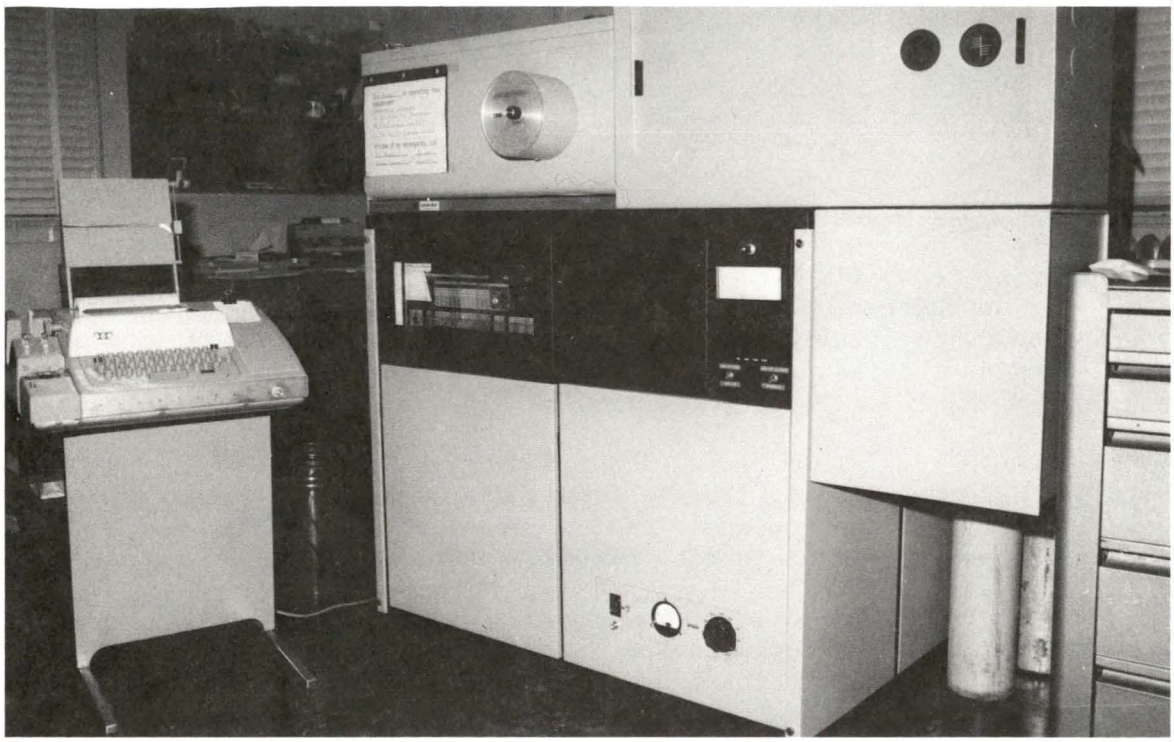


FIGURE A-1. - Computer-controlled direct-reading spectrograph.

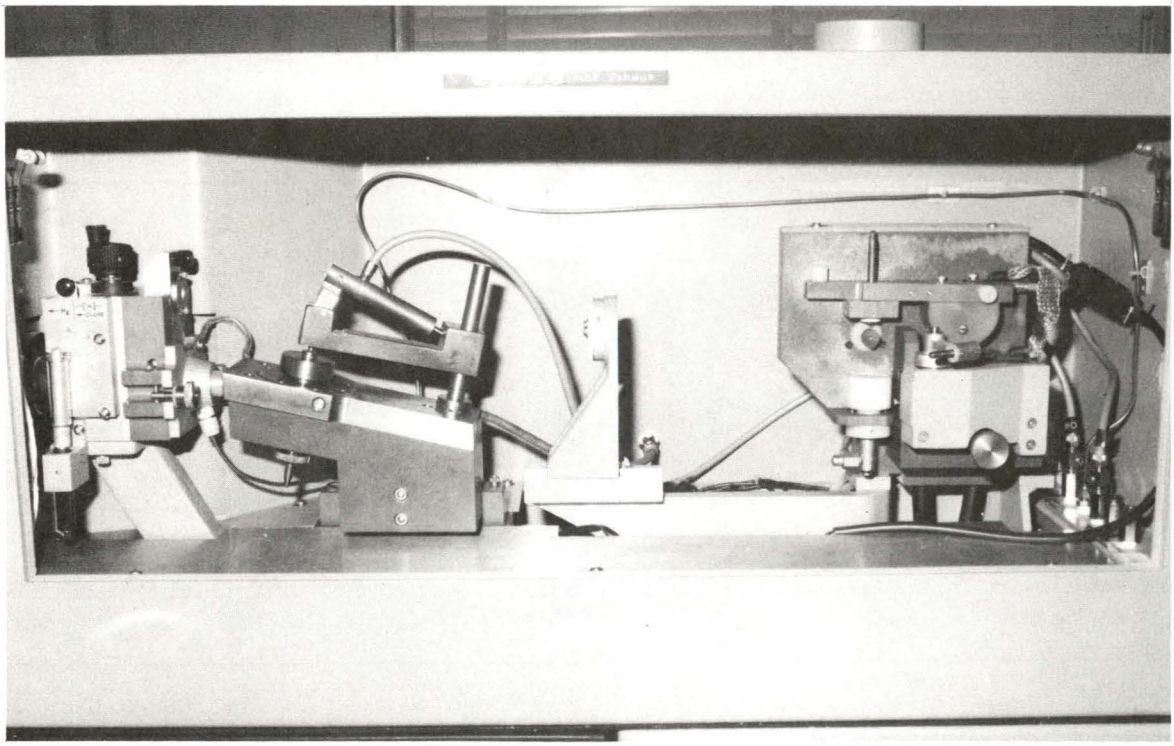


FIGURE A-2. - Interior of excitation stand.

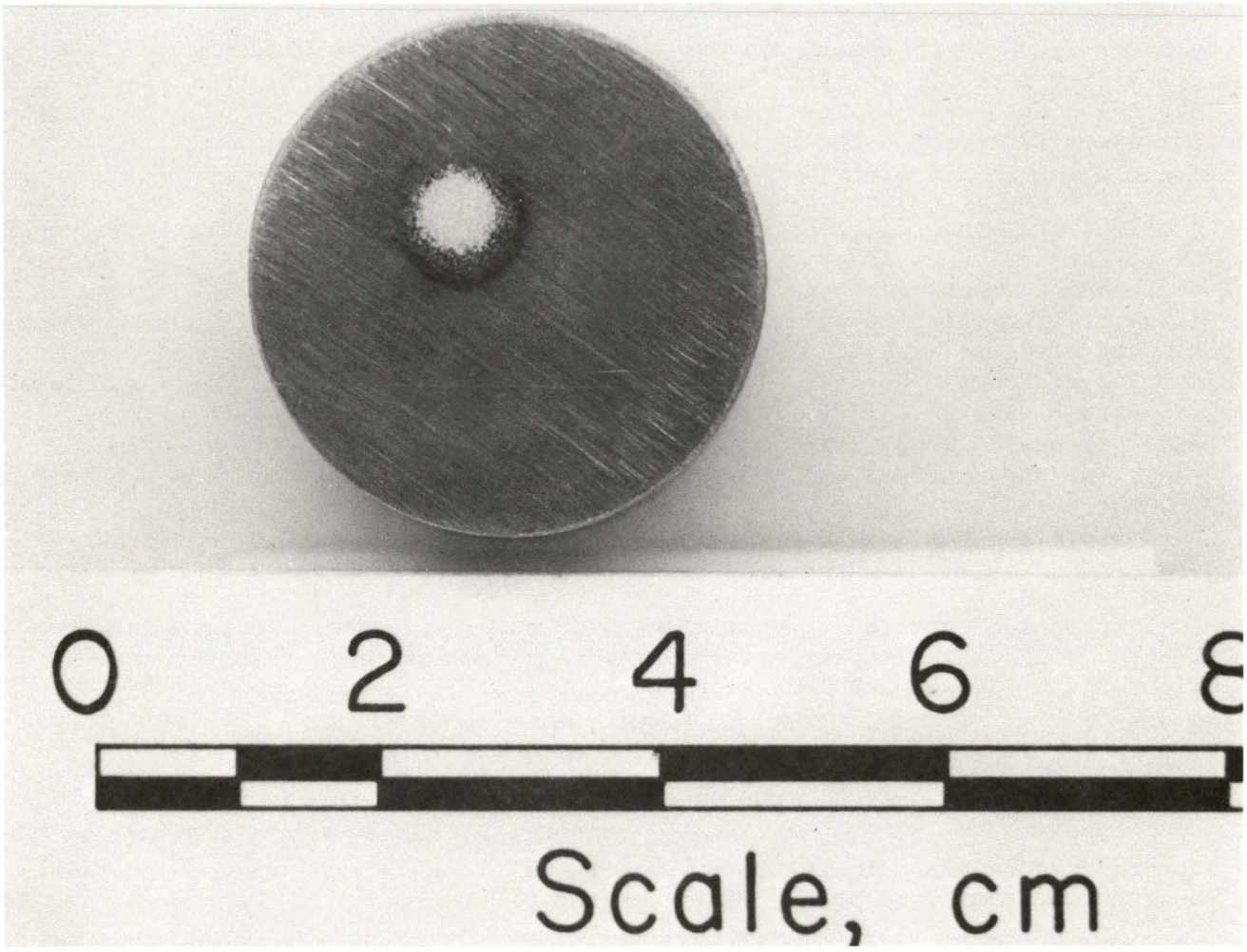


FIGURE A-3. - Sample surface showing burn.

It was observed that above 3 pct iron the reproducibility of analytical results became increasingly erratic. An examination of the Cu-Fe phase diagram showed that the iron precipitated out of solid solution at low levels. However, the sample preparation method used retained iron in the copper in a form that could be accurately and reproducibly determined up to about 3 pct iron. If the iron concentration exceeded this amount, the sample was dissolved and analyzed by X-ray emission techniques.

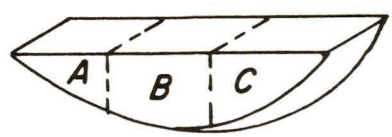
Sample Preparation

The spectrochemical analysis of solid copper is made more difficult because component elements react to form intermediate phases, rather than single-phase solid solutions. Thus, elements have different energy

relationships with each other. Since bonding energy can vary from atom to atom, it requires different amounts of energy to excite one atom as opposed to another atom of the same element. Phase relationships are critical not only in sample analysis, but also in physical characteristics such as electrical conductivity and heat conductivity. Conductivity in turn affects the element volatility rates in spectral excitation. Analytical results could also vary depending upon the physical dimensions and materials of the molds used to prepare samples and upon the type of surface used for spectrochemical analysis.

To overcome these problems, it was decided to prepare samples by a controlled chill-casting technique. By solidifying the metal as quickly as possible, segregation could be greatly minimized. In unidirectional solidification, segregation occurs essentially at the top of the button in cooling, and microstructure formation is uniform at the chilled sample face. This approach correlated with the analytical need of the researcher to take molten on-stream samples and obtain analytical results within 10 min. The following procedure was used to obtain direct-reader samples. A ceramic ring, 1 inch high by 1-1/2 inches in ID by 2-1/4 inches in OD, was placed upon a cooled copper plate. A spoon of molten copper was drawn from the furnace or from the pour, and the ceramic ring was two-thirds filled with the molten copper. The solidified copper button was then water-cooled, and the surface to be analyzed was prepared by grinding on an 80-grit silicon carbide rotating belt.

To obtain representative samples from copper pigs that contained over 5 pct iron, a slice approximately 2 inches thick was taken from the center section of the pig and cut into sections A, B, and C:



The three sections were melted separately in an induction furnace, and sample buttons were prepared by the chill-casting technique.

Standardization and Analysis

It was necessary to obtain iron-in-copper standards covering the expected analytical range from 0.1 to 5.0 pct. Ideally, the standards should have a physical and metallurgical history similar to that of the samples to be analyzed. Standards with these specifications were not commercially available, so chill-cast buttons that had been submitted for direct-reader analyses were analyzed by atomic absorption spectrophotometry or by X-ray emission techniques to establish iron concentration. Five chill-cast buttons were analyzed, with the following results (in pct Fe): 0.23, 0.73, 1.38, 2.20, and 4.10. Using these samples as standards, the direct reader was programed for the determination of iron in copper. The operating parameters follow:

Wavelengths:	
Fe	3,020.64 A.
Cu	4,022.63 A.
Flush gas	Argon.
Preburn	10 sec.
Exposure	20 sec.
Source conditions:	
Capacitance	0.01 μf.
Inductance	310 μh.
Frequency	2 breaks per 1/2 cycle.

The final product of the smelting operation was copper pigs. The precipitation of iron from copper was particularly apparent in a study for iron segregation in the copper pigs. When the pig slices were polished for analysis, metallic iron prills could be seen in the top of the pigs, a band of smaller prills could be seen in the middle, and comparatively little iron was seen in the bottom. Not only did the direct-reader analyses show this, but these areas could be roughly defined by using a hand magnet, which first detected iron at a concentration of about 3 pct. Increasing iron caused greater magnetic attraction. All copper pigs did not show extreme segregation. A typical analysis of a nonsegregated pig showed a range of iron from 3.5 to 4.1 pct.

During this investigation, the iron contents of metal samples that were analyzed ranged from 0.1 to 15 pct. The overall accuracy and reproducibility obtained by these analytical techniques did not exceed 3 pct.

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