RECOVERY OF COPPER FROM SMELTER SLAGS

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Abstract

This paper presents the results of experiments carried out to study the possibilities of recovering copper from the dump smelter slags. Direct leaching of copper with (i) ammoniacal solutions of ammonium carbonate and (ii) neutral ferric sulphate solutions was investigated but the recovery of copper was low. Sulphatising roast gave much better extraction and a recovery of 55–56% was obtained. The non-extractable copper is inferred to be in solid solution in the smelter slag.

Introduction

The copper resources of our country are exceedingly limited, especially in comparison with our annual consumption which is of the order of thirty to forty thousand tons.[1] The copper smelter at Ghatsila barely meets 25 per cent. of the requirements, and apart from the Copper Belt in Bihar, no new economic deposits of copper are reported. The demand for copper will increase with years and as the richer ores get depleted, recovery will have to be made from complex lean ores and from waste products such as the dump smelter slags.

It is true that with modern methods of operation, the copper losses in slags have been reduced to a minimum; nevertheless, the slag from the reverberatory furnaces contains 0·3 to 0·7 per cent. copper which is a potential source of the metal provided the slag admits of relatively cheap concentration. This project was therefore undertaken with a view to develop a suitable economic method for recovering copper from the waste slags. For this investigation, the slag was obtained from the Indian Copper Corporation's smelter at Ghatsila.

Experimental

Analysis of Slag.—The dump slag, as received, was in the form of dark grey, stony lumps. A representative sample of eight pounds was obtained by coning and quartering. It was crushed in a jaw crusher and subsequently ground to minus 120 mesh in a porcelain ball mill.

The slag was difficult to decompose by acid digestion and therefore an oxidising fusion, as recommended by Kinnunen,[2] was adopted for opening it. The fused mass was treated with sulphuric acid to fumes in order to dehydrate silica. The various slag-constituents were then estimated in the acid-extract by the standard methods.

On account of the very low percentage of copper in the slag, this constituent was determined colorimetrically as the deep blue cuprammonium complex, using the Klett-Summerson Photo-Electric Colorimeter.

Sulphur was determined separately by digestion of the slag in *aqua-regia* and its precipitation as barium sulphate.

Table I records the composition of the slag.

TABLE I. *Slag-Composition*

Constituent	%
Copper	0·636
Sulphur	0·816
Silica	35·92
Iron oxide, FeO	53·83
Alumina	7·07
Lime and Magnesia	1·728 (by difference)

There is a great deal of divergence of opinion as regards the manner in which copper occurs in the slag. It was formerly thought that all the copper was in the form of mechanically entrapped matte but Wright's[3] work on the settling and elutriation of slag disproves this and it would seem that losses are due more to solution rather than entrapment of the matte. Grabill[4] has made a distinction between physical and chemical losses in slag. Physical losses arise from imperfect smelting, inadequate difference in the specific gravity of the matte and slag, and gas flotation of matte particles, while chemical losses may result from the formation of copper oxide and pellets of metallic copper. The results of Lathe[5] indicate that fifty to seventy-five per cent. of the copper in the slag is present as oxide or silicate, while Jackman and Hayward[6] contend that there is no evidence for the existence of silicate in the slag. To sum up the position, it would seem that copper may be present in the reverb slag in one or more of the following forms: (*a*) matte, either in suspension or in solution, or both, (*b*) copper oxide, (*c*) pellets of copper, and (*d*) copper silicate.

Literature survey indicates that several attempts have been made for recovering copper from slags and among the methods studied are: (i) Leaching the slag with ammoniacal solutions,[7] (ii) Treatment of the molten slag with matte containing a small percentage of copper,[8] (iii) Displacement of copper by fusion with metallic iron,[9] and (iv) separation of entrained sulphide particles by flotation,[10] but full details of the procedures adopted are not available. In this study, two methods of recovery were investigated, namely, (*a*) leaching to dissolve the copper values in the slag, and (*b*) roasting to convert copper into the water-soluble sulphate.

Leaching Studies on Copper Slag.—A good leaching agent, apart from being cheap and easily available, should be specific in its action, be effective in cold, dilute solution and be easily regenerated at the end of the operation so that it may be recycled. Two of the more common reagents that satisfy these requirements and which have found extensive application in the hydrometallurgy of low-grade copper ores, are ammoniacal solutions of ammonium carbonate and neutral or acidified solutions of ferric sulphate. The ammoniacal lixiviants are effective on oxidised copper ores and on metallic copper[11] whereas solutions of ferric sulphate are particularly suitable for leaching low-grade sulphide ores[12] and when acidified, these solutions are known to dissolve the oxides of copper also.[13]

The experiments on leaching were carried out by agitation-leaching. For this purpose, a known weight of the pulverised slag (minus 120 mesh) was placed in a pyrex container and covered with the lixiviant. The container was fitted with a glass-stirrer and thorough agitation of the pulp was ensured by rotation of the stirrer by means of a variable speed, fractional horse-power motor. The pulp was withdrawn at definite intervals of time, the residue thoroughly washed and the copper in the leach determined colorimetrically after making up the filtrate to 250 c.c. In the case of ammoniacal leach, copper was estimated directly on the colorimeter whereas in ferric sulphate leach, it was necessary to separate the iron before estimating copper. In order to minimise the loss of copper due to occlusion on the ferric hydroxide, the hydroxide was dissolved in dilute sulphuric acid and reprecipitated with ammonia. The purpose of hydrogen peroxide in the ammoniacal leachants was to oxidise any cuprous compounds present. The results of the leaching tests are set forth in Tables II and III.

TABLE II. *Lixiviation of Copper from Slag with Ammoniacal Solutions*

Weight of slag taken for each test 8 gm. Copper content of the slag .. 50·88 mgm.

Sl. No.	Composition of leachant						Time of leaching hrs.	Copper extracted mgm.	Percentage extraction
	NH_4OH			$(NH_4)_2CO_3$		H_2O_2 (Peroxyl) 20 volumes c.c.			
	4 N c.c.	2 N c.c.	N c.c.	2 N c.c.	N c.c.				
1	100	..	..	..	..	..	8	10·6	20·83
2	100	..	..	..	..	10	8	10·6	20·83
3	..	..	..	100	..	..	8	10·1	19·85
4	..	..	..	100	..	10	8	11·0	21·59
5	50	..	..	50	..	..	4	12·7	24·93
6	50	..	..	50	..	10	4	13·0	25·55
7	50	..	..	50	..	10	8	16·8	32·99
8	50	..	..	50	..	10	16	17·0	33·39
9	25	..	..	75	..	10	8	16·8	32·99
10	75	..	..	25	..	10	8	16·8	32·99
11	..	50	..	50	..	..	4	12·5	24·56
12	..	50	..	50	..	10	4	12·7	24·93
13	..	50	..	50	..	10	8	16·8	32·99
14	..	..	25	..	75	10	4	10·6	20·83
15	..	..	75	..	25	10	4	10·6	20·83
16	..	..	50	..	50	10	4	10·6	20·83
17	..	..	50	..	50	10	8	13·4	26·30

TABLE III. *Lixiviation of Copper with Ferric Sulphate*

Weight of slag for each test .. 8 gm. Weight of copper in the slag .. 50·88 mgm.

Sl. No.	Concentration of the leachant %	Time of leaching hrs.	Copper extracted mgm.	Percentage extraction
1	0·125	1	5·47	10·74
2	0·125	2	6·33	12·44
3	0·125	3	6·62	13·00
4	0·125	6	6·72	13·19
5	0·250	1	7·68	15·08
6	0·250	2	8·45	16·60
7	0·250	3	8·83	17·34
8	0·250	6	8·83	17·34
9	0·500	1	8·93	17·52
10	0·500	2	9·40	18·47
11	0·500	3	9·40	18·47
12	0·500	6	9·51	18·66
13	1·000	1	9·40	18·47
14	1·000	3	10·10	19·83
15	1·000	6	10·10	19·83
16	2·000	1	9·60	18·86
17	2·000	6	10·10	19·83

Conclusions.—(i) A consideration of the results shows that leaching with neutral ferric sulphate and ammoniacal solvents does not give a high extraction of copper from the smelter slags. Recovery is of the order of 20 per cent. in the case of sulphate leach and 33 per cent. for ammoniacal leach.

(ii) Since ferric sulphate dissolves primarily copper sulphides and metallic copper whereas ammoniacal leachants are capable of dissolving native copper and oxidised ores but not copper from the sulphides, it is inferred that the slag contains copper both in the oxidised condition and as sulphide.

(iii) It appears that the low extraction with ferric sulphate is due to the occurrence of copper sulphide matte in dissolved state which form does not admit of easy extraction by solvent action. This is further confirmed by studies on roasting of the slag for sulphatisation as given subsequently.

(iv) The extraction with the two solvents is more a function of time than of concentration.

Sulphatising Roast.—Roasting of copper ores for sulphatisation has been suggested as a preliminary step in the hydro-metallurgical recovery of copper. It is known that if a mixture of iron and copper sulphides is roasted in air, it is the burning of iron sulphide which is responsible for the primary elimination of sulphur as sulphur dioxide. The ferric oxide formed as a result of this reaction acts to catalyse the formation of sulphur trioxide. With increasing formation of sulphur dioxide and the consequent increase in the concentration of trioxide, the copper oxide gets sulphatised unless the temperature is so high as to favour decomposition of the sulphate.[14] Ashcroft[15] has pointed out that reactions in roasting lead primarily to the formation of sulphates, iron oxide with silica acting as a catalyst in the formation of sulphur trioxide. Copper sulphate is more stable than iron sulphate so that by adjustment of the temperature and the partial pressure of sulphur trioxide in the roaster, it would be possible to sulphatise copper and form insoluble iron oxide. The principal advantage of such a separation would be the formation of water-soluble copper sulphate and an insoluble gangue. Two methods suggested themselves for this extraction, (i) Roasting with ferric sulphate in order to convert the oxidised and sulphur-bearing copper into sulphate, and (ii) Roasting of the slag to oxide and its subsequent sulphatisation to form copper sulphate with minimum formation of iron sulphate.

Sulphatising Roast with Ferric Sulphate.—The roasting experiments were conducted in a 18″ long × 1″ internal diameter, nichrome wound silica tube furnace. Temperature of the furnace was regulated by a variable resistance and the temperature measurements were made using a chromel-alumel thermo-couple.

A weighed quantity of the – 120 mesh slag was intimately mixed with ferric sulphate in the ratio 4: 1, placed in porcelain boats and introduced into the furnace. The tube of the furnace was plugged at both ends with rubber corks carrying glass outlet tubes.

A slow steady stream of air from an air cylinder, freed from moisture by passing through a sulphuric acid bubbler, was passed during the course of the roasting in order to maintain an oxidizing atmosphere. The rate of flow of air was measured with a flow-meter. The exit gases from the furnace were absorbed in alkali and a trap was provided to guard against back suction.

At the end of the experiment, the boats were removed from the furnace and the roasted slag was extracted with water. Copper was estimated colorimetrically in the extract, after removing iron as ferric hydroxide.

A second series of experiments was conducted with the slag previously roasted in a current of air to oxidise all sulphides to the oxides. The calcined slag was then ground with ferric sulphate and the experiments repeated as before. The influence of temperature, period of roasting, and rate of flow of air on the efficiency of sulphatisation was studied.

The results of these experiments are presented in Tables IV and V:—

TABLE IV. *Experiments on Roasting with Ferric Sulphate Without Previously Calcining the Slag*

Weight of slag for each test	.. 4 gm.
Weight of anhydrous ferric sulphate added	.. 1 gm.
Weight of copper slag ..	.. 25·44 mgm.

Sl. No.	Temp. of roasting ° C.	Period of roasting min.	Rate of flow of air c.c./min.	Amount of copper sulphatised mgm.	Percentage extraction
1	500	90	40	7·39	29·12
2	550	90	40	9·21	36·18
3	600	90	40	7·96	31·27

TABLE V. *Experiments on Roasting with Ferric Sulphate After Calcining the Slag in Air at* 500° C.

Weight of slag for each test	4 gm.
Weight of ferric sulphate added	1 gm.
Weight of copper in slag	25·44 mgm.

Sl. No.	Temp. of roasting ° C.	Period of roasting min.	Rate of flow of air c.c./min.	Amount of copper sulphatised mgm.	Percentage extraction
1	500	90	10	8·64	33·94
2	500	90	40	8·45	33·19
3	500	150	10	9·40	36·93
4	550	90	10	10·90	42·81
5	550	90	40	10·90	42·81
6	550	150	10	11·50	45·16
7	600	90	10	9·21	36·18
8	600	90	40	8·93	35·07
9	600	150	10	9·98	39·20

Conclusions.—A consideration of the results shows that

(i) Under the conditions studied, the maximum conversion obtained is 45% when the slag is first oxidised in a stream of air and then roasted in admixture with ferric sulphate at 550° C. for two and a half hours. Direct roasting with ferric sulphate without a prior oxidising roast, gives an extraction of about 36% under similar conditions.

(ii) The recovery is improved if the slag is calcined before sulphatisation which suggests that copper sulphide is more resistant to sulphatisation than oxidised copper.

(iii) Temperature has a definite influence on the extent of sulphatisation. The yields of copper sulphate are maximum for 550° C. An explanation for the lower recovery above and below this temperature can be found in the reduced dissociation of ferric sulphate at the lower temperatures and the greater tendency for copper sulphate to decompose when temperatures are high.

(iv) An increase in the rate of flow of air during sulphatisation does not improve the formation of copper sulphate.

Differential Sulphatisation.—The decomposition of a sulphate or its formation from oxide at any temperature is determined by its dissociation pressure at that temperature. If the partial pressure of sulphur trioxide superimposed on the system is greater than the equilibrium partial pressure P_{SO_3}, the oxide will get sulphatised, and if less than the equilibrium value, decomposition of the sulphate will be favoured. The stability of a sulphate is therefore dependent on the temperature and partial pressure of sulphur trioxide to which it is subjected. It is therefore seen that if two sulphates have different dissociation pressures for any specific temperature, it would be possible by imposing a pressure of sulphur trioxide, intermediate between the dissociation pressures of the two sulphates, to sulphatise one of the oxides leaving the other in the oxidised condition.

The smelter slag consists primarily of iron silicate, alumino-silicates and copper in the oxide and sulphide condition. It was therefore thought desirable to investigate this process of selective sulphatisation as a means of separating the copper in the form of water-soluble sulphate, leaving iron and aluminium in the oxidised condition. No data are available on the sulphatisation of iron and aluminium silicates and therefore, the method selected was to pass sulphur dioxide and air in diverse proportions and at different temperatures over the slag in order to sulphatise copper to the maximum exclusion of iron and aluminium sulphates. The slag was given an oxidising roast before attempting sulphatisation.

Experimental.—The roasting experiments were carried out in a silica tube-furnace and the details are shown in Fig. 1. Sulphur dioxide was stored

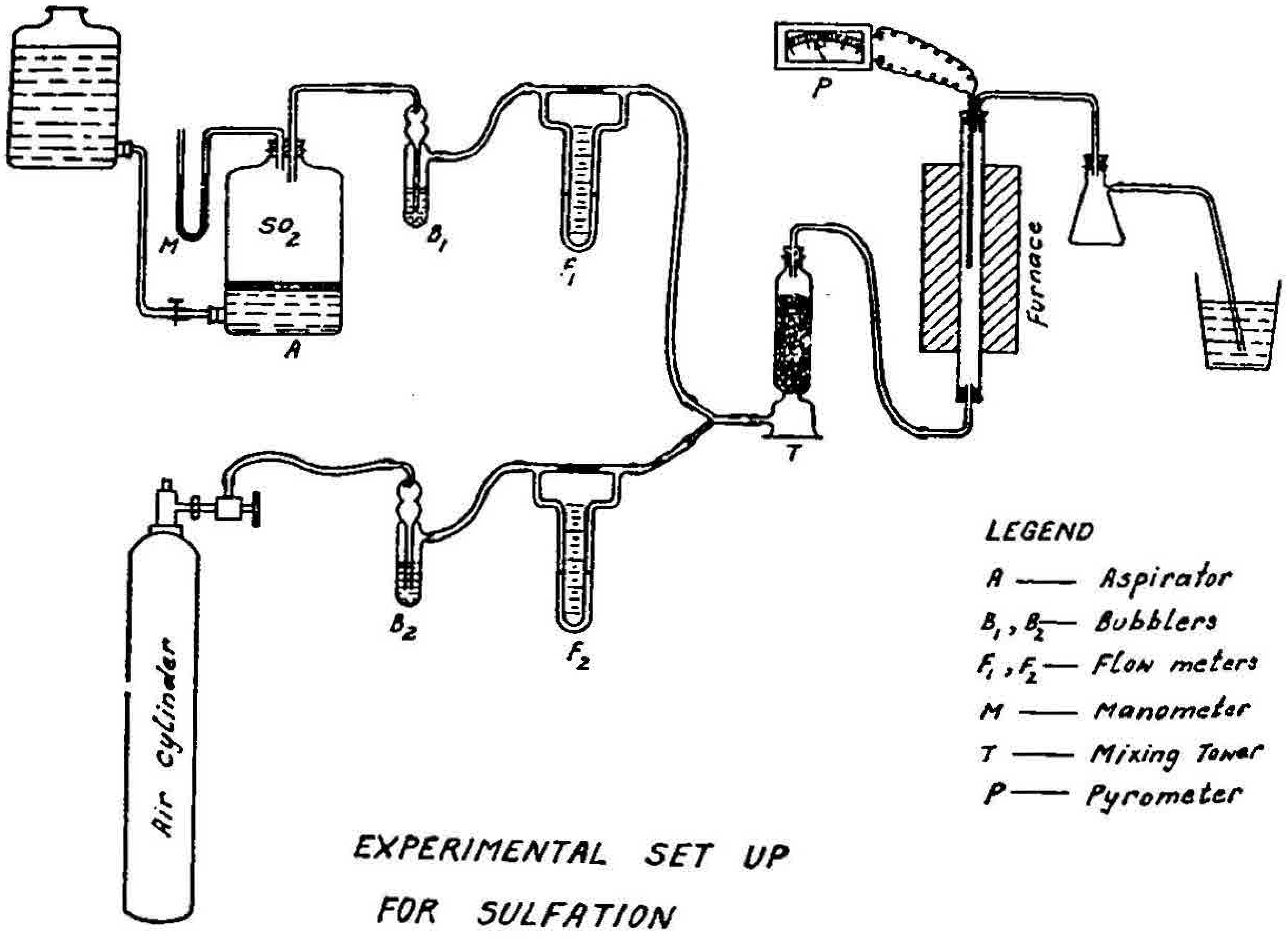

FIG. 1

in the aspirator marked 'A' which contained water over which was kept a layer of liquid paraffin in order to prevent direct contact between the gas and water. The gas was displaced from the aspirator by introducing water from a second aspirator, and any moisture contained in the sulphur dioxide was removed by bubbling it through sulphuric acid. The rate of flow was measured by means of a calibrated flowmeter F_1 included in the circuit. Air, tapped from a compressed air cylinder, was dried before passing it to the tube-roaster *via* the flow-meter F_2. The gases were mixed in the tower T packed with glass-wool.

The tube-roaster was wound with nichrome and the temperature inside the furnace was measured by means of a calibrated pyrometer. In order to preheat the gases, the lower eight-inch length of the tube furnace was packed with broken pieces of fire-clay, over the top of which was kept a pyrex glass-wool compact. A weighed quantity of the reverb slag was placed on the compact and the gases passed vertically in the upward direction in order to promote better gas-slag contact.

The sulphur gases from the exit end were led into a dilute solution of alkali in order to absorb them and a trap was provided to prevent back-suction.

Before passing sulphur dioxide, the slag was given a strong oxidising roast for ninety minutes at 500° C. in a current of air and subsequently sulphatisation was carried out using different temperatures and sulphur dioxide to air ratios. At the end of the experiment, the calcines were allowed to cool in a stream of sulphur gases and the solid products were recovered and leached with water. Copper in the extract was estimated colorimetrically, after removing any iron present. Experiments were conducted to study the influence of (i) temperature and (ii) concentration of sulphur dioxide in the gases, on the yield of copper sulphate.

Table VI shows the results from these sulphatisation studies.

After roasting the slag for four hours at 600° C. in an atmosphere of sulphur dioxide and air mixed in the proportion 1 : 2, and then dissolving out the copper sulphate formed, the residue was again subjected to the same sulphatising conditions but no further recovery of copper was obtained.

From an examination of the results, it is inferred that:

(i) In the range of temperature 600–650° C. as much as 56% of the copper contained in the slag is sulphatised. A sulphur dioxide-air ratio of 1 : 2 is ideal for efficient conversion.

TABLE VI. *Sulphatising Roast of Slag in an Atmosphere of Sulphur Dioxide and Air*

Weight of slag for each test	..	3·6 gm.
Weight of copper in slag	..	22·90 mgm.
Time of roasting	.. ..	4 hours.

The P_{SO_3} values—under column 5—were calculated from the thermodynamic data, given by K. K. Kelley,[16] for the equilibrium reaction $2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$.

Sl. No.	Temp. of roasting ° C.	Ratio of SO_2: air	Rate of flow of gases c.c./min.	Partial pressure of SO_3 mm.	Amount of copper sulphatised mgm.	Percentage recovery
1	500	1 : 2	50	138	8·35	36·44
2	550	1 : 1	40	167	9·60	41·91
3	550	1 : 2	50	217	10·3	44·94
4	550	1 : 4	50	96	9·98	43·56
5	550	1 : 6	50	88	9·21	40·21
6	600	1 : 1	40	167	12·7	55·42
7	600	1 : 2	50	177	12·9	56·30
8	600	1 : 4	50	123	12·5	54·57
9	600	1 : 6	50	80	11·3	49·33
10	650	1 : 1	40	130	12·6	54·99
11	650	1 : 2	50	130	12·9	56·30
12	650	1 : 4	50	97	12·2	53·25
13	650	1 : 6	50	56	11·1	48·45
14	700	1 : 2	50	88	11·2	48·87

(ii) Even at the lower temperatures and with lower proportions of sulphur dioxide, it would be possible to obtain the same degree of sulphatisation provided sufficient time is allowed.

The absence of further conversion of copper to the sulphate—when the residue is again roasted under sulphatising conditions—suggests that the residual copper is protected from the action of sulphurous gases. It is likely that this residual copper exists in solid solution in the iron silicate, which can be verified from a petrographic examination of the slag.

Conclusion.—The low recovery of copper from the leaching experiments indicates the complex character of the slag which does not permit of easy solution of metal values. Yet, the comparatively high conversion as a result of the more drastic treatment with sulphur trioxide points out that the slag is sufficiently responsive for an efficient recovery of the locked-up copper to be possible. The encouraging results from the sulphatisation studies. presented in this paper, suggest the feasibility of economic recovery of copper, utilising the waste sulphur gases from the smelter. The studies indicate that iron is not sulphatised except to a minor extent, and further work is in hand to determine the conditions for its complete elimination in the sulphatised product.

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