# Continuous production of copper from concentrates

## J. SCHMIEDL, J. HOLECZY and F. SEHNALEK

THIS paper presents the basic techniques and research results on pyro-metallurgical continuous production of copper from sulphide concentrates.

Production of copper from sulphide flotation concentrates accounts for about 75% of the total production of the metal. The standard techniques adopted for this purpose had attained a good measure of engineering proficiency but attempts were made to develop better methods and in the 1950's new techniques for concentration smelting of copper mattes were established, such as the cyclone smelting process developed in the USSR and investigated at the Metal Research Institute at Panenske Brezany in Czechoslovakia, and two interesting techniques for autogenous matte smelting : the INCO and OUTO KUMPU process which treats copper concentrates in converters (Hitachi techniques) and the continuous conversion of mattes into white mattes in a system developed by Prof. Diomidovsky.

The continuous conversion process is now being studied in Australia, (WORCRA process) and in Canada at the Noranda Research Centre.

The present trends are broadly as follows:

- Development and application of autogenous smelting process.
- 2. Switching over to smaller units with higher smelting and production capacities.
- 3. Application of continuous processes.

While considering the possibilities of developing a new continuous copper production technique from flotation sulphide concentrates, we proceeded from the assumption that to be successful the new technique should basically incorporate all the above features. Accordingly, we first examined the possibilities of continuous conversion of copper mattes to do away with the standard practice involving two stages in the operation.

#### Continuous conversion of copper mattes

During the last century there has been no outstanding

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## SYNOPSIS

The paper deals with the continuous treatment of sulphide copper concentrates. This work was linked up to the investigation of copper matte treatment.

The work was carried out on a pilot plant. The output of the model operation was limited by the installed sources of pressure air and by the oxygen ramp.

Two test campaigns of several weeks duration were carried out with concentrates of the following composition :

- (a)  $13^{\circ}3^{\circ}_{\circ}$  Cu, 29.1% Fe, 27.0% S, 3.1% CaO, 2.7%  $Al_2O_3$ , 0.6% MgO, 13.4% SiO<sub>2</sub>.
- (b) 14.0% Cu, 29.8% Fe, 30.2% S, 6.6% SiO<sub>2</sub>, 2.7%Al<sub>2</sub>O<sub>3</sub>, 1.7% MgO, 0.2% CaO, 4.2% Zn, 3.5%As, 1.2% Sb.

To attain a shorter starting time, copper matters of the following compositions were used :

41.8% Cu, 27.0% Fe, 25.5% S or 59.9% Cu, 7.2% Fe, 23.6% S.

Both these mattes possessed more than 1 per cent nickel. Examples of the composition of the blister copper obtained and the slag composition are given in the paper.

Direct copper recovery from the (b) concentrate is 94.7 per cent without depreciation of slag. When the slag is depreciated, e.g, to 0.3 per cent of Cu, the recovery can be increased to 97.7 per cent. Oxygen utilization exceeded 90 per cent.

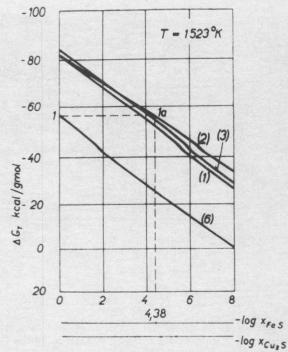
An experimental unit, of 10 tons copper concentrate per day capacity, is now in operation. It is provided with a device for pre-heating blast and a dust separator. The unit can undertake the long test runs with various kinds of copper concentrates, including polymetallic ones. It is possible to treat samples of about 100 tons of concentrate. The unit is provided with measuring and control instruments.

development in the design of converters for copper production and conversion of mattes is still carried out in horizontal or vertical converters running intermittently.

Intermittent treatment brings about frequent shut downs resulting in great heat losses. Temperature fluctuations in the converter lining reduce its life. More iding periods are required for maintenance of the converter i.e. for patching or relining. Hermetic sealing of the converter nose has not yet been realised satisfactorily which hinders the effective utilization of heat, sulphur dioxide and dusts of the exit gases. The Hoboken type converter (Belgium) with sealed nose is an exception. From design point of view its disadvantage is that it requires a special flue which must allow the rotation of the converter.

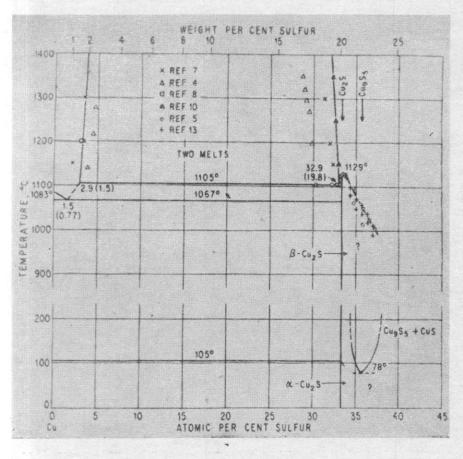
The main drawback of the present converters is the imperfection of the blast inlet system which restricts the amount of the blast supplied, causes rapid wear of lining in the zones of blowers and necessitates considerable physical labour for cleaning them in spite of the mechanization of this operation which has been recently reported by Noranda, McGill and Chino<sup>2,5</sup>.

The basic theoretical problem of continuous converting was the determination of conditions for a simultaneous course of the basic oxidation reactions of both the conversion stages i.e. FeS and Cu<sub>2</sub>S. We therefore, made a thermodynamical study of the standard conversion process. From the values of free enthalpies of

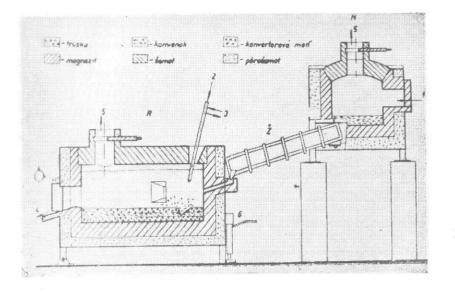


- Relation between free enthalpies of oxidation reactions in the converter on concentration of FeS and  $Cu_2S$   $Fe_2S+3/2 \ O_2 = FeO+SO_2$   $9/10 \ FeS+3/2 \ O_2=3/10 \ Fe_3O_4+9/10 \ SO_2$   $FeS+3/2 \ O_2+1/2 \ SiO_2=1/2\cdot2 \ FeO.SiO_2+SO_2$   $Cu_2S+3/2 \ O_3=Cu_2O+SO_2$ 1
- (2)
- (4)

(3)



Phase diagram of the Cu-S system 2 showing limited mutual solubility<sup>12</sup>



3 Diagram of the plant R continuous converter Z connecting channel N smelting furnace

oxidation reactions of matte conversion it is possible to determine conditions under which oxidation of FeS and  $Cu_2S$  will take place simultaneously (Fig. 1). These problems are dealt in more details in the papers 6, 7, 8, 9 and 10 cited in reference. These reactions result in iron oxides which together with the quartz present form slag and copper oxide, and after the converter reaction has taken place, converter copper is produced.

Converter slag, white matte and converter copper form a system of three liquid phases, mutually miscible only to a limited extent. The specific weight of converter slag at 1200°C ranges from 3.22 to  $3.62 \text{ g/cm}^3$ ; the specific weight of white matte (80% Cu) at 1200°C is  $5.2 \text{ g/cm}^3$  and that of copper at 1200°C is  $7.8 \text{ g/cm}^{3.14}$ With a suitable choice of slag composition, such that it is not too viscous, separation into individual phases in the above mentioned system can be expected to proceed quickly.

Copper solubility in the converter slag has not yet been precisely determined. However, it may be assumed that it is not of a higher order than tenths of a per cent and it has been proved that it is a function of temperature.<sup>11</sup> Slag solubility in copper matte need not be considered for our present purposes.

During conversion, converter copper is formed only when the matte consists mostly of Cu<sub>2</sub>S. In this process, Cu<sub>2</sub>S is first saturated with copper and it is only afterwards that copper saturated with Cu<sub>2</sub>S is separated in an individual phase (Fig. 2). The diagram shows that as long as there is white matte present in the system, the separated converter slag will contain about 1.8% S (according to other authors 0.8–0.9%).

On the basis of these theoretical considerations, in 1959 we started building an equipment for continuous conversion of copper mattes. The design of this equipment was taken over from D. A. Diomidovsky<sup>13</sup> who published in 1959 his research results on intermittent top-blowing of copper mattes in an enclosed through. The detailed designs of our experimental set-up was determined by two aspects—by the autogenesis of the

process and the necessary minimum volume of the molten mass and secondly, by the efficiency of the installation corresponding to minimum space requirements for settling of the slag. The output of the experimental plant was 6–7 tons of copper matte per 24 hours; the copper content in the treated matte varied from 41 to 44%. The last testing model roughly corresponds to Fig. 3 and it is shown in Figs. 4 and 5.

The plant was furnished with auxiliary burners for its preheating at the beginning of experiments and for heating during shut-down periods. Basically, the plant was designed for treatment of molten matte supplied from a smelting furnace through an opening in the rear wall of the converter. Air was blown into the melt under a pressure of 6 atm. through blowers inserted in the roof of the continuous converter. In the roof near the blowers there was also an opening for charging quartz which was batched by an adjustable batcher according to the amount of air blown in and the composition of combustion products.

In accordance with theoretical assumptions the converter copper produced was of a suitable quality. Several analyses of the converter copper produced in one of the experimental campaigns are listed in Table I.

TABLE I Chemical composition of converter copper

| ample | Cu % | Ni % | S %  |
|-------|------|------|------|
| 5     | 98.0 | 0.86 | 0.83 |
|       | 97.8 | 0.91 | 0.94 |
|       | 98.1 | 0.85 | 0.89 |
|       | 97-1 | 1.02 | 1.16 |
|       | 96.9 | 1.5  | 1.35 |

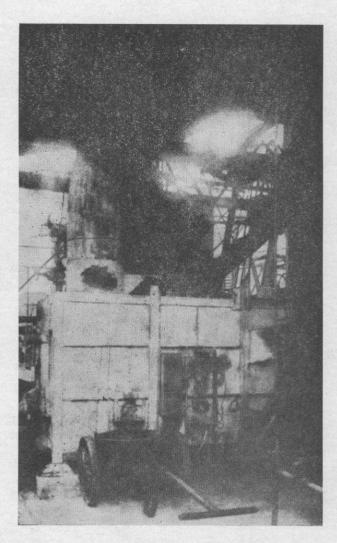
4 The continuous copper matte converter

The copper content in slag depends, to a great extent, on settling conditions which are directly dependent on the operational procedure. Typical analyses of the slag obtained are shown in Table II.

TABLE II Chemical composition of converter slags

| Sample | Cu % | S %  | Fe % | SiO <sub>3</sub> % |
|--------|------|------|------|--------------------|
| 6      | 1.25 | 0.20 | 47•8 | 23.6               |
| 7      | 0.88 | 0.22 | 43.5 | 27.4               |
| 9      | 0.99 | 0.30 | 42.1 | 27.3               |
| 11     | 0.92 | 1.10 | 51.3 | 21.2               |
| 16     | 0.64 | 0.10 | 46.2 | 27.2               |

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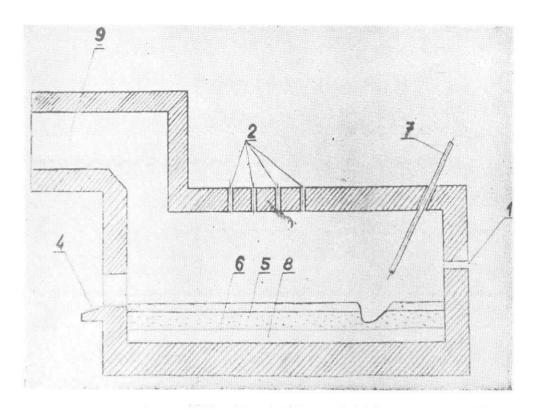


5 Another view of the continuous copper matte converter

Converter slags containing higher copper contents are, as a rule, those which are taken directly from the converter with a scoop. The slag samples taken from the overflow hole were of lower copper content. It is obvious from Table II that slags produced in continuous conversion even on pilot scale, are much poorer in copper than those from common converters. It may be assumed that in a large scale production plant where conditions for slag settling are better, the copper content in the slag would be even lower.

The middle layer in continuous conversion comprises white matte with a slight iron content. How-ever, the iron content of the middle layer, in the period when the system is almost stabilized and when copper is produced, is essentially higher than the theoretical content. The expected amounts of the main elements in the middle layer reached values shown in Table III.

The utilization of air according to the entire material balance reached 81% while extraordinary deteriorations in air exploitation during the failure of blowers were not taken into account.



- 6 Diagram of the furnace 1 auxiliary burners 2 charging holes 3 slag discharging hole 4 copper matte
  - 5 slag
  - 6 pressure blower device
  - 7 copper
  - 8 gas outlet

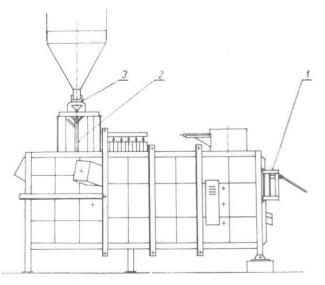
| TABLE | Ш | Chemical   | composition | of | the | middle | layer | during |
|-------|---|------------|-------------|----|-----|--------|-------|--------|
|       |   | conversion |             |    |     |        |       |        |

| Sample | Cu % | S %   | Fe % |
|--------|------|-------|------|
| 10     | 72.2 | 20.1  | 6.13 |
| 14     | 77.9 | 17.8  | 2.40 |
| 17     | 78.9 | 16.9  | 1.40 |
| 20     | 81.8 | 12.8  | 0.90 |
| 35     | 79-7 | 14.18 | 1.20 |

The equipment developed and the technology for continous conversion of copper mattes has the following advantages over the traditional techniques :

- 1. The equipment is suitable for continuous process shut down times are eliminated, heat losses are minimized and thermal shocks are practically eliminated.
- 2. As the lining can be protected with a garnish, the equipment may have theoretically unlimited life. The zone of the highest temperatures in the equipment is in the centre of the melt while in the standard converters this zone is immediately against the wall which is thus enormously thermally stressed.

- 3. Feeding of the material into the set can be carried on continuously and, mainly, without
- 4. The slags formed have a comparatively small copper content. We have found out that these



- 7 Diagram of the installation
  - 1 slag discharging hole
  - 2 blowers
  - 3 charging of the concentrate

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slags can be further treated conveniently (flotation).

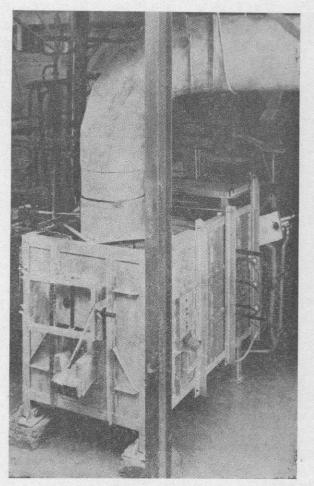
5. The set enables better exploitation of the raw material—copper mattes. It can be hermetically closed so that no losses occur either in sulphur or converter dust. It is of importance that  $SO_2$  content in combustion products can be high (near theoretical composition) and steady. The new equipment makes possible a better utilization of pysical heat of the combustion products.

## Direct copper production from sulphide copper concentrates

Our investigation on continuous treatment of sulphide copper concentrates has been linked up with the work on continuous treatment of copper mattes.

Sulphide copper concentrates are very similar to copper mattes in their chemical composition. When they are heated in presence of oxygen, dissociation of higher sulphides takes place and also a partial oxidation until the concentrate melts down and matte and slag are formed. In our considerations on the possibility of direct pyro-metallurgical production of copper we can therefore apply a similar theoretical analysis of the problems as in case of continuous treatment of copper mattes, i.e. in principle it is a question of simultaneous separation of sulphur and iron by oxygen in the system Cu-Fe-S-O-Si.

In order to overcome the disadvantages of the common method of converter copper production consisting of agglomeration, concentration smelting and converting, in the year 1962 we developed direct production of converter copper from sulphide concentrates by continuous treatment in a smelting furnace.<sup>15</sup> In this process copper bearing material is charged into the smelting furnace where it is smelted to produce slag and matte. The matte is oxidized by oxygen enriched air which is blown from the top and introduced by means of blowers to produce converter copper and slag. The oxygen content in the blast is dictated by the thermal balance of the equipment, or by the requirements for SO<sub>2</sub> concentration in combustion products. Just as in continuous conversion, three liquid phases are to be formed in the equipment. The upper one, the slag layer, must not be too thick so as not to resist much the blast to enter the melt. The middle layer, actually formed by the white matte, is the biggest, and at the bottom of the equipment is a layer containing copper. Since dissociation of minerals and liberation of gaseous sulphur take place in smelting of copper concentrates, the remainder of the oxygen in the furnace space can be employed for their oxidation. The equipment (Fig. 6) is preheated<sup>1</sup> before starting operation. Then the concentrate together with the fluxes, is charged through the charging holes.<sup>2</sup> Smelting of concentrates by auxiliary burners is carried out till the melt fills the furnace up to the slag discharging hole,<sup>4</sup> wherein copper mattes<sup>5</sup> and slag<sup>6</sup> are produced. When the slag rises to the level of slag discharging hole, it starts flowing out of the set continuously. Afterwards auxiliary burners are stopped and inserted into the

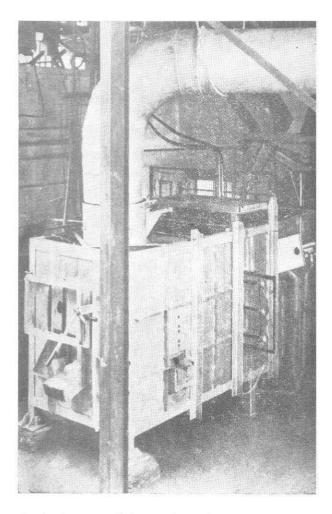


8 Installation for direct production of the converter copper from sulphide copper concentrates

pressure blower device<sup>7</sup> and the process similar to that in standard continuous conversion can start. Advantages of this converter copper production are obvious. However, a very unfavourable feature of the equipment, shown in Fig. 6, is the great amount of flue dust from the charge.

Therefore, for model testing of the technique devised arrangements were made for charging granular sulphide copper bearing charge with fluxes, along with the reaction pressure blast.<sup>16</sup> When using this technique, the granular material is blown into the melt in such a way that it is all the time covered by a protective cone of the pressure blast, thus fully preventing any formation of mechanical flue dust.

The construction of the equipment has been developed from the continuous converter. The size of the equipment was determined not only in respect to the heat balance but also and especially from the standpoint of technological features of the equipment (separation of the individual layers). The pressure of the blast ranged from 4 to 6 atm., the blast of air was enriched with oxygen up to 42%. The production capacity of the set up was about 6 tons of copper



9 Another view of the installation for direct production of converter copper from sulphide copper concentrates

concentrates per 24 hours. A diagram of this plant is shown in Fig. 7 and actual photographs in Figs. 8 and 9.

Two experimental campaigns of several weeks duration were carried out. The concentrates treated were of the following compositions :

- A : 13.3  $^{o_{0}}_{~~o}$  Cu, 29.1 % Fe, 27.0 % S, 3.1% CaO 2.7  $^{o_{0}}_{~~o}$  Al $_{2}O_{3}$ , 0.6% MgO, 13.4 % SiO $_{2}$
- B: 14.0 % Cu, 29.8% Fe, 30.2% S, 6.6% SiO<sub>2</sub> 2.7 % Al<sub>2</sub>O<sub>3</sub>, 1.7% MgO, 0.2% CaO, 4.2% Zn, 3.5 % As, 1.2% Sb.

To attain shorter starting periods, copper mattes of the following compositions were used :

41.8 % Cu, 27.0% Fe, 25.5% S, or 59.9 % Cu, 7.2% Fe, 23.6% S Both mattes contained more than 1% Ni.

The concentrate was dried up to 4% moisture. The flux used was quartz sand containing 99.2% SiO<sub>2</sub>. Approximately 90% utilization of oxygen of the blast

was attained in the tests. Examples of the converter copper produced are shown in Table IV.

| TABLE IV | Chemical | composition | of | converter | copper |  |
|----------|----------|-------------|----|-----------|--------|--|
|----------|----------|-------------|----|-----------|--------|--|

| Sample | Cu %  | Ni % | Fe % | S %  |
|--------|-------|------|------|------|
| 16     | 96.42 | 1.26 | 0.24 | 0.93 |
| 80     | 97-34 | 0.80 | 0.75 | 0.82 |
| 100    | 98.24 | 0.60 | 0.43 | 0.70 |
| 106    | 97.34 | 0.72 | 0.43 | 1.10 |
| 110    | 97.64 | 0.20 | 0.62 | 0.93 |

Copper was tapped from the equipment discontinuously; slag flowed out continuously.

Examples of slag composition are given in Table V.

| TABLE V Chemica | composition | of | converter | slags |  |
|-----------------|-------------|----|-----------|-------|--|
|-----------------|-------------|----|-----------|-------|--|

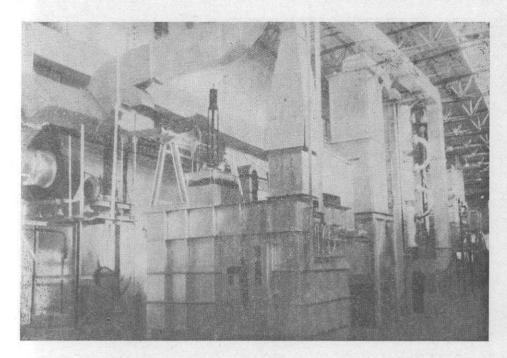
| Sample | Cu % | S % | Fe % | SiO2 % |
|--------|------|-----|------|--------|
| 12     | 16   | 0.4 | 48.1 | 25.6   |
| 50     | 1.3  | 0.7 | 45.6 | 25.7   |
| 62     | 0,9  | 0.1 | 45.6 | 32.9   |
| 92     | 1.1  | 0.3 | 49.6 | 25.5   |
| 95     | 1.1  | 0.2 | 45.0 | 28.6   |

Examples of the matte layer composition are shown in Table VI.

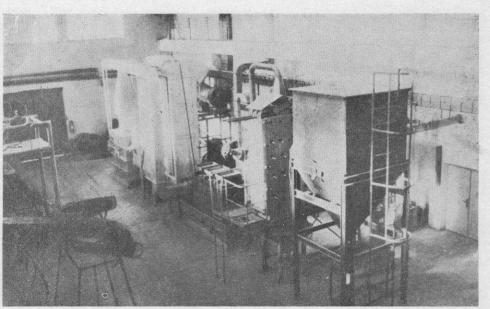
TABLE VI Chemical composition of converter mattes

| Sample | Cu % | S %  | Fe % |
|--------|------|------|------|
| 17     | 72:6 | 18.6 | 1.4  |
| 20     | 77.1 | 18-1 | 0.5  |
| 79     | 72 5 | 19.9 | 2.2  |
| 98     | 77.8 | 20.2 | 0.3  |
| 105    | 78.2 | 18.4 | 0.1  |

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10 General view of the experimental unit

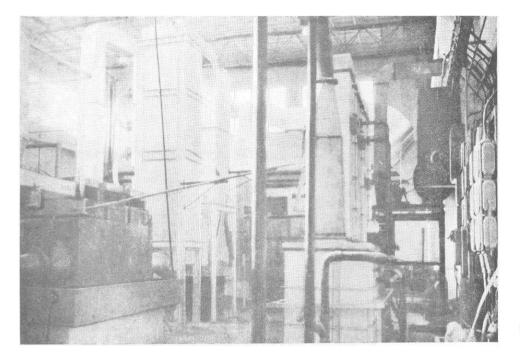


11 Another view of the experimental unit

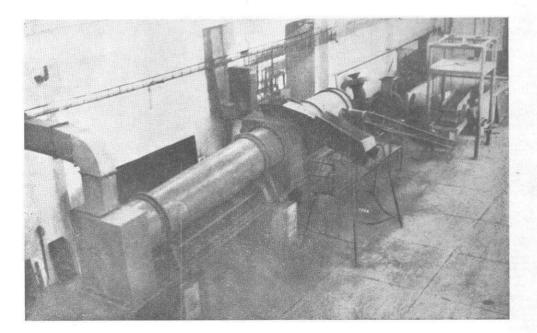
The compositions of the individual products obtained in the treatment of mattes and concentrates are practically the same. There is a difference in the copper contents of slags; the average copper content in slags formed in direct copper concentrate treatment is a little higher—by about 0.2%. This can be explained by the fact that in the above campaigns production was carried out with a relatively thin slag layer so that the conditions for segregation of the mechanically stripped white matte were not favourable. The average content of  $SO_2$  in waste gases varied according to the amount of  $O_2$  employed. Waste gases are almost completely utilised; they contain a high percentage of  $SO_2$ .

The object of our experiments was mainly to establish the practical feasibility of the new technique developed for direct production of copper from sulphide copper bearing raw materials. It may be said that this objective has been achieved successfully.

At present we are trying to increase copper recovery



12 Side view of the experimental unit



13 Installation for preparation of charge

by treating slags, although the new technique ensures considerably lower copper losses than the standard process.

### Conclusion

For a more comprehensive and detailed study of the continuous process, especially with respect to the determination of the entire material balance, as well as for the study of thermo-technical balance, we have developed an experimental unit with a capacity of 10-12 tons of concentrate per 24 hours (Figs. 10, 11, 12, 13). It is equipped, with an air preheating device, (autogenous process), and arrangement for blast enrichment (reaction rate, concentration of SO<sub>2</sub> in gases). The unit permits long-term experimental campaigns with various kinds of copper concentrates, including polymetallic ones. Final tests are planned for the year 1969.

The advantages of this new technique are especially apparent when we realise that the common practice for copper production from flotation sulphide concentrates consists of three or, at least, two stages, namely :

- 1. Eventual desulphurization roasting,
- 2. Concentration smelting for production of matte,
- 3. Conversion of mattes.

If these operations are carried out in separate units, two intermediate products (sinter matte) and three kinds of gases, flue dust, reclaimable converter slag and waste slag are produced.

Such a technique involves high capital costs and labour, while copper recovery remains high due to a number of losses.

On the other hand, the new technique developed ensures autogenous process, a small plant of large output and continuity of the process which is the basic condition for its automation.

The unit is also of a very simple stationary design. Basically, it is a reverberatory furnace, which enables some pyroselection, i. e. a better exploitation of the valuable accompanying elements. In the treatment of the concentrate of composition "B" we have attained 94.7% efficiency of copper recovery without slag depreciation.

In conclusion, it may be said that introduction of this technique in production plants may have a revo-lutionary effect on converted copper production, since in addition to these advantages it promotes productivity while capital and production costs are lowered.

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## Discussions

Mr C. V. Sundaram (Bhabha Atomic Research Centre, Bombay): The author has stated that direct conversion is achieved in a reverberatory type furnace. Can he kindly clarify how the air or oxygen is supplied to the matte phase to achieve the conversion to blister copper?

Dr Ing. J. Schmiedl (Author) : Air or oxygen are blown

into the melt under pressure. The pressure depends on the distance of the blower from the melt and on the height of the sample layer. The blast must move away the slag layer and enable a direct contact of air or oxygen with the middle matte layer. Air, under pressures of up to 6 atm, was used in the experiments described.