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Application of Emission and Absorption Spectroscopy for Characterization of a Copper Converting Process

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The emission and absorption spectra of a copper converter flame have been investigated. It was found that the emission spectra consisted of Planck radiation and superimposed discrete structures. The band structure was dominated by PbS in the slag-making stage and by PbO in the copper-making stage. Towards the end of the slag-making stage the ratio of the PbO and PbS band intensities (PbO/PbS) changed, in good agreement with thermodynamical calculations. Absorption measurements were performed during the copper-making stage, where the absorption edge of SO_2 at about 380 nm was the dominating feature. The implications of these measurements for process steering and control are discussed.

Index Headings: Emission spectroscopy; Absorption spectroscopy; Process control; Copper converter diagnostics.

INTRODUCTION

Emission and absorption spectroscopy have been used in different types of chemical analyses for several decades. There are a large number of commercial products based on these techniques. Although these techniques are well established in laboratory environments, they are not commonly applied for monitoring, steering, and control of industrial processes in harsh environments with dust, particles, heat, and severe vibration. To our knowledge, emission and absorption spectroscopy have been applied to the characterization of a copper converting process for the first time in the present investigation. Emission spectroscopy has previously been applied in the steel industry,[1] and it has recently been applied to temperature measurements in a coal furnace using the OH emission.[2] The present experiments were carried out at Boliden Metall AB.

In its natural form, copper is present mainly in combination with sulfur. The most common copper mineral is chalcopyrite ($CuFeS_2$). Many other metals (Fe, Pb, Zn) are often present as sulfur compounds together with copper minerals. The Cu content in the ore may be as low as about 1%. Following mining, the copper content is increased to 15–30% Cu in a concentration plant.

In the first metallurgical step in the copper production process the concentrate is heated to about 600°C, whereby about one-third of the sulfur content of the concentrate is converted into sulfur dioxide (SO_2). The concentrate is then smelted in an electric smelting furnace at 1200°C. In the smelting process, the material divides into two layers. The upper layer, the slag, carries the rock and the metal oxides (mainly Fe, Zn, and Pb). The lower layer, the matte, consists of those metals which are still bound to sulfur (above all, copper and iron, but also some zinc and lead). The copper content in the matte is about 44%.

The molten matte is charged into a converter for conversion to blister copper. In addition to the matte, the converter is charged with sand and copper scrap. The purpose of this conversion is to remove iron, sulfur, and other impurities from the matte, thereby producing liquid metallic copper. This is achieved by injecting oxygen-enriched air into the molten matte at a high temperature (1150–1250°C). The blister copper, the copper content of which being about 98%, is further refined by metallurgical means and electrolysis.

The conversion process, which is the main subject of the present study, is performed in two distinct steps, namely, the slag-making stage and the copper-making stage. In the former stage the sulfur bound to, above all, Fe, Zn, and Pb is oxidized. Later, Fe reacts to form FeO and Fe_3O_4. Zn and Pb largely follow SO_2 in the process gases. The slag-making stage is complete when the FeS in the matte has been almost completely converted to oxides, and before Cu_2S has begun to form metallic Cu. The slag, containing about 20%-by-weight magnetite, is removed at various times during the slag-blowing stage. The principal product of this stage is "white metal," consisting of liquid Cu_2S containing about 77% copper.

In the copper-making stage the remaining sulfur is oxidized to SO_2. Copper is not appreciably oxidized until it is almost devoid of sulfur; thus the blister copper product is low in both sulfur and oxygen.

In industrial operations the matte is added to the converter in two or more steps. The resulting slag is removed from the converter after each step and new matte is added. In this way the amount of copper in the converter gradually increases until the quantity is sufficient for a final copper-blow. The converting process should be terminated when the sulfur content is below 0.1% in the liquid copper.

The conversion of copper matte generally takes place in a cylindrical converter about 10 m long and 4 m in diameter (cf. Fig. 1). The molten matte is charged into the converter through a large opening (3 × 2 m²), and the air is blown into the matte via a row of nozzles along the length of the converter. During this process large amounts of hot gases, containing sulfur dioxide (10–15%) and vaporized metals (lead and zinc), are emitted via the converter opening. The process gases also contain a large amount of particles. Since the temperature in the converter is about 1200°C, there is intense black-body radiation from the ejected particles and some radiation from vaporized material.

The optical spectrum emitted from a flame is related to the temperature and the chemical composition of the

flame. By studying the color and the shape of the flame above the converter mouth, a trained operator can gain information about the conditions in the converter, and, above all, he or she can tell when the blasts should be interrupted. A correct determination of these points is indeed very critical. If the slag-making stage is interrupted too early, the impurities (Ni, Sb) will remain in the white metal instead of being absorbed by the slag. These impurities will be troublesome in subsequent processes. On the other hand, if the blow is continued too long, the white metal will start to transform into liquid Cu. This will result in a higher Cu content in the slag, leading to a loss in Cu; furthermore, the liquid Cu collects impurities (e.g., As and Sb) very efficiently. Again, this factor will cause problems in subsequent steps. Regarding the copper-making stage, it is essential to continue the blow long enough to let the impurities reach the slag phase. If the blow lasts too long, the result will be that liquid Cu transforms into CuO. While the full converter process lasts for 8 to 9 h, the end-point determination should be correct to better than one minute. This precision is difficult to achieve, even for a skillful operator, and an "objective" determination would be valuable.

It is reasonable to believe that by using fast optical techniques it would be possible to extract considerably more information from the emitted radiation than is possible with the naked eye. The motivation for the present study of the copper converting process was to investigate whether

(1) there are characteristic features in the emitted radiation that can be registered rapidly and reliably by optical means;
(2) these emission characteristics change during the process in a way that gives information on the conditions in the process;
(3) the changes in emission characteristics can be used for process control in practice;
(4) emission spectra of minority impurities are present;
(5) absorption spectroscopy, particularly on SO_2, can provide additional information relevant to process control.

With these questions in mind, we have registered and analyzed emission and absorption spectra during the slag-making and copper-making stages of the copper converting process at Boliden Metall AB. In addition, laboratory experiments have been performed to help in the interpretation of the converter data.

EXPERIMENTAL SETUP

The experimental setup for measurements on the copper converter is shown schematically in Fig. 1. In the emission measurements light from the luminous exhaust gases was imaged onto the entrance slit of a spectrograph (Jarrel-Ash Model 1233) by means of a quartz lens (f = 20 cm). The spectrograph was equipped with three gratings with 150, 600, and 2400 grooves/mm. The possibility of observing the spectra at different resolutions greatly facilitated detailed temporal studies and elemental analyses. The detector was a proximity-focused linear diode array (EG&G Model 1420) consisting of about 750 intensified diodes (each 25 μm × 2.5 mm) and sensitive in
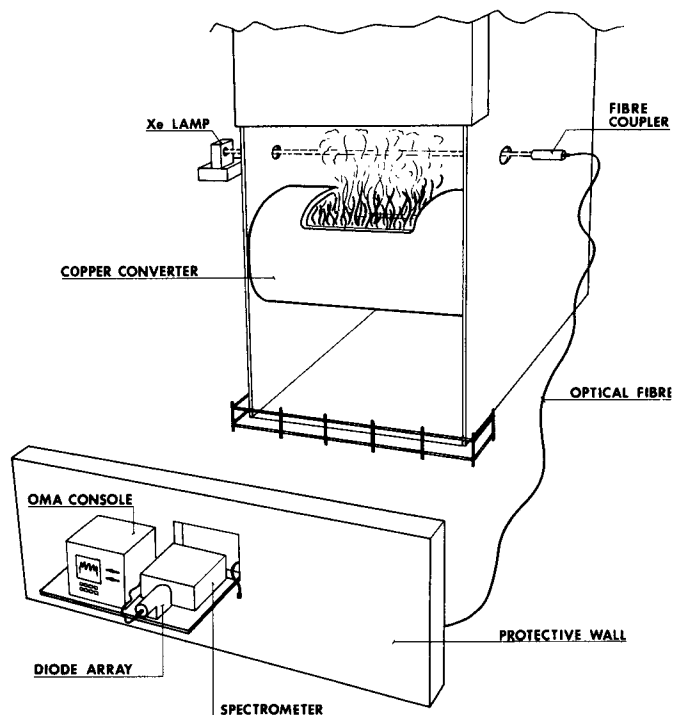

FIG. 1. Experimental arrangement for the emission and absorption measurements on the copper converter.

the 200–800 nm wavelength region. The spectra were displayed live on a PARC 1460 detector console and stored on floppy disks for further processing.

In the absorption experiments a high-pressure xenon lamp with high brightness in the ultraviolet wavelength region was used. The lamp was placed at the focus of a spherical mirror, thus producing a parallel light beam through the exhaust gases above the converter mouth. A quartz lens mounted on an x-y-z translator directed the transmitted light into one end of an optical fiber. The fiber was a 600-μm-thick, about 30-m-long quartz fiber, protected against mechanical damage by a surrounding plastic tube. The other end of the fiber was positioned in front of the entrance slit of the spectrograph. The absorption spectra were displayed and stored in the way described for the emission experiments.

MEASUREMENTS AND RESULTS

In the present measurements on the copper converter the main emphasis was on the emission experiments. The direct observation of the emission from the converter constituted a single-ended passive technique. The absorption measurements required an external lamp and some kind of receiving telescope connected to a quartz optical fiber. The harsh industrial environment, with vibration, high temperatures, large amounts of dust and particles, and limited optical access, made the absorption technique a little less attractive.

Emission. Emission spectra were recorded during both the slag- and the copper-making stages. During the more interesting periods of the process cycle, one spectrum per minute was usually recorded. The converter flame was very bright, and the time required to obtain a spectrum with a sufficient number of counts was very short, typ-
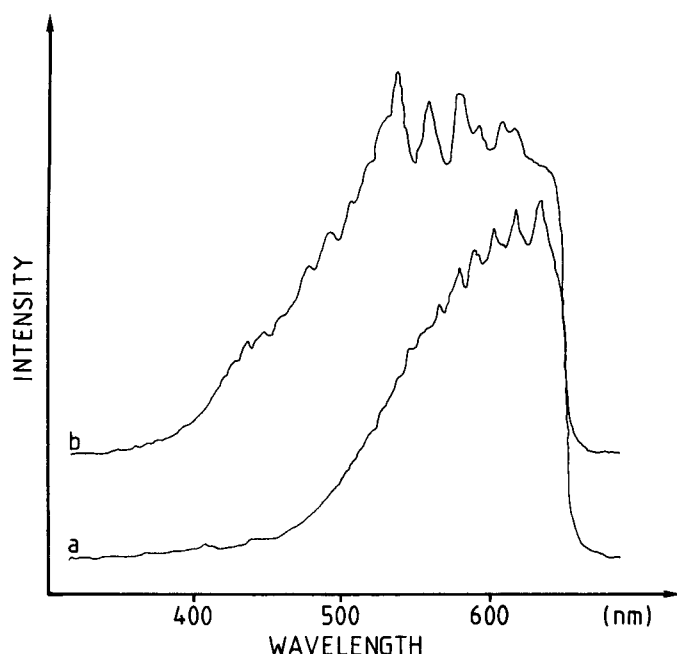
FIG. 2. Emission spectra from the converter flame at low resolution. Spectrum (a) is from the slag stage and spectrum (b) originates from the copper stage.
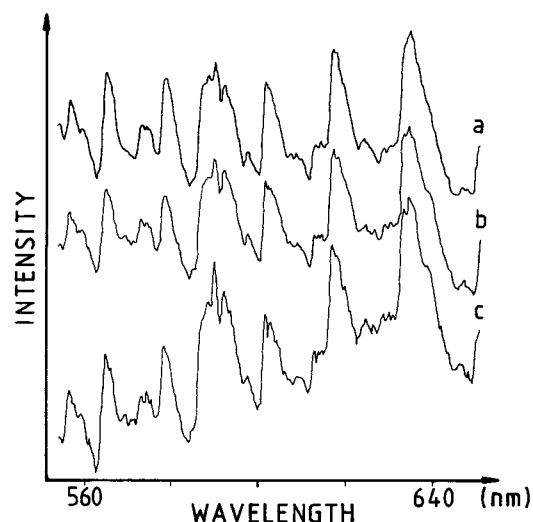

FIG. 3. Spectra from two different slag-blowing cycles at medium resolution. Spectra (a) and (b) are from the beginning and the end of the same stage, while spectrum (c) is from a completely different process cycle.

ically 10–100 ms. Normally 100 scans were averaged, which means that the total exposure time for each spectrum was approximately 1–10 s.

The spectral ranges covered in one exposure by the three gratings were 3200 Å, 800 Å, and 200 Å, respectively. The coarse grating was used to obtain an overview of the spectra, while the highest resolution was used for detailed studies of the emitted light. The recordings were wavelength-calibrated relative to superimposed Cd, Hg, and Na spectra emitted from discharge lamps. In some exposures, in particular when the high-resolution grating was being used, no calibration lines were available. However, sufficient overlap with neighboring exposures, together with knowledge of how the dispersion varies with wavelength, made an accurate calibration of these recordings possible. The wavelength determinations are accurate to 0.5 Å, which was found to be sufficient for unambiguous classification of most of the observed features.

The spectral distribution of the radiation from the converter flame observed at low resolution is shown in Fig. 2. Spectrum (a) shows the emission during the slag-making stage and spectrum (b) the emission during the copper-making stage. None of the spectra shown in this paper have been corrected for the wavelength-dependent sensitivity of the detection system. The abrupt drop in intensity around 650 nm is due to the limited physical dimensions of the intensifier.

A major contribution to the total emitted intensity comes from Planck radiation from particles and also, to some extent, from the rear wall of the converter housing. Complex discrete features are superimposed on the Planck curves. These features are different for the two stages but remain more or less stable during a full blast. Furthermore, the discrete features remain essentially unchanged from one cycle to another, as illustrated by the

spectra given in Fig. 3. The three spectra, recorded at medium resolution, represent two different slag-making cycles. Spectra (a) and (b) are recordings from the beginning and end of the same slag-blow, while spectrum (c) was recorded during a different cycle. The very good agreement between the three curves, even in the finer details, is striking, particularly in view of the fact that the content of the converter varies from one cycle to another. These observations gave a positive answer to our first question, namely, whether there are characteristic features in the emitted radiation that can be registered rapidly and reliably by optical means. Bearing in mind the violent nature of the copper-converting process and the flames above the converter, the stability and the reproducibility of the emitted spectrum are remarkable.

The low- and medium-resolution spectra discussed so far did not allow any decisive identification of atomic and molecular species in the converter flame. Therefore the 400–600 nm wavelength range was also recorded with the 2400 grooves/mm grating. Typical high-resolution spectra from the slag-making and the copper-making stages can be seen in Figs. 4 and 5. Each of the spectra shown is constructed from about fifteen individual exposures, each covering some 20 nm. The spectra are not corrected for the varying sensitivity of the detector system.

Figure 4 shows that during the slag-making stage the discrete features contribute a substantial part to the intensity emitted in the visible wavelength range. The two very narrow structures around 590 nm are the sodium D_2 and D_1 lines at 589.0 nm and 589.6 nm. The two components are well resolved, indicating a resolving power better than 0.5 nm. The intensity of the sodium lines relative to the rest of the discrete spectrum decreases slowly during the process.

It has not been possible to identify with certainty any atomic lines besides the sodium lines. The remaining structures all have the typical shape of molecular vibrational-rotational bands. The majority of the bands are degraded towards longer wavelengths. A comparison with
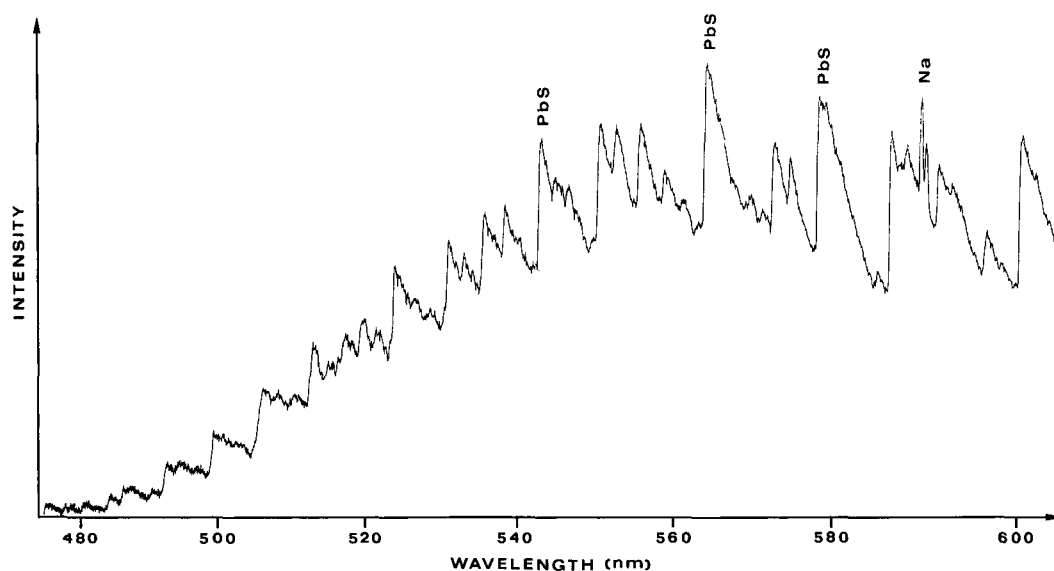
FIG. 4. High-resolution spectra from the slag stage. The strongest PbS bands and the Na lines are indicated.

published data on molecular spectra[3] shows that the dominant emitter during the slag-making stage is PbS. A few of the more prominent bandheads are indicated in Fig. 4. In total, 34 vibrational bands have been identified in the A-X and B-X systems of PbS. Qualitatively, the relative intensities of the bands are in agreement with published data.[4] Only a few very weak structures cannot be positively ascribed to PbS.

The emitted spectrum during the copper-making stage (Fig. 5) is quite different from the slag-stage spectrum discussed above. Significantly fewer particles are emitted during the copper-blow, and the overall light emission is lower, by a factor of four to five. Also, the discrete spectrum is drastically different. The PbS bands which dominated the slag-stage spectrum are no longer present. One of the dominant emitters during the copper-making stage was shown to be PbO. In all, 28 bands in the A-X and B-X systems of PbO have been identified from compar-

isons with published data on this molecule.[3] The relative intensities of the bands are in qualitative agreement with data available in the literature.[5] A few of the stronger PbO bands are indicated in Fig. 5.

After the PbO bands had been identified, a number of very strong emission bands remained unidentified. The relative intensities of the PbO bands and the unidentified bands vary appreciably from one process cycle to another and also change gradually during the blow. A detailed analysis of the spectrum shows that the CuCl molecule is responsible for most of the unidentified bands. The ten strongest bands included in the tables of Pearse and Gaydon[6] are all present on our recordings. In addition to the PbO and CuCl bands, only the sodium lines and a few weak molecular bands are present.

The observed change of the relative strengths of the PbO and PbS bands during the full converter cycle agrees qualitatively with the results of thermodynamical cal-
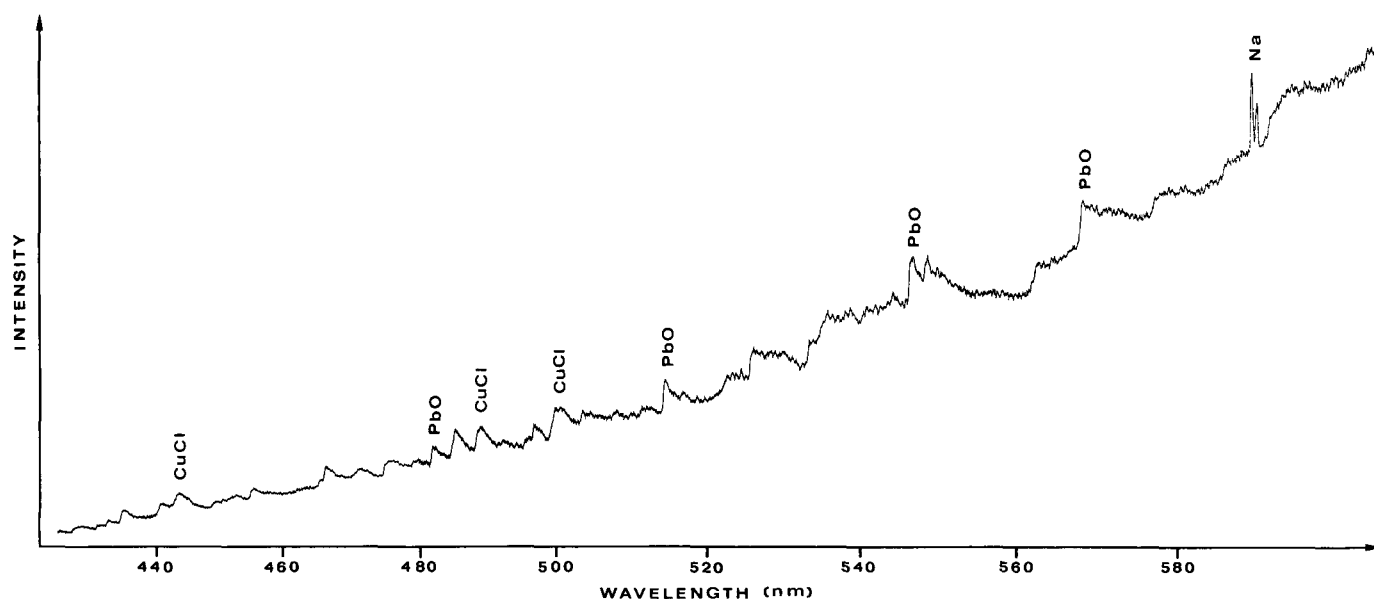

FIG. 5. High-resolution spectra from the copper stage. The strong PbO and CuCl bands are marked, together with the Na lines.
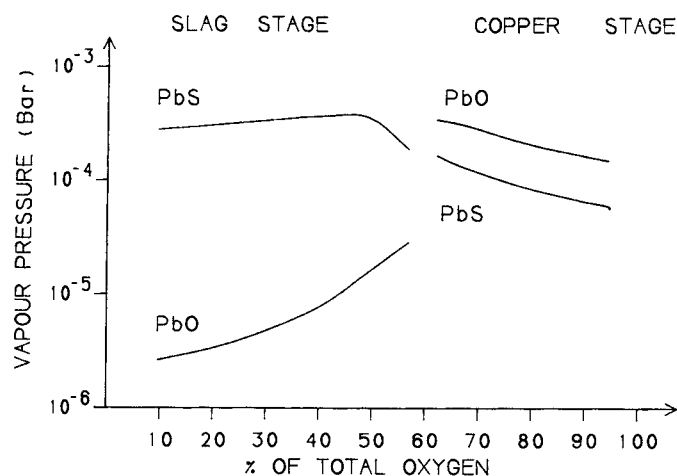
FIG. 6. Calculated vapor pressures of PbS and PbO just above the surface of the melt vs. the amount of oxygen used during the slag and the copper stages.

FIG. 7. A plot of the observed PbO/PbS ratio vs. time close to the end of the slag stage.

culations. The calculated PbO and PbS vapor pressures as a function of the total amount of oxygen added are displayed in Fig. 6. As the addition of oxygen is more or less constant in time, the horizontal scale can be regarded as a time scale. The calculations are based on thermodynamical data, assuming equilibrium conditions just above the surface of the molten metal. The diagram shows that the PbS vapor pressure decreases and the PbO vapor pressure increases as the end of the slag-making stage is approached. These calculated relative changes in the vapor pressures correspond to relative changes in the strength of the observed emission from PbO and PbS. Close to the end of the slag-stage, the intensity of the PbO bands increases in comparison with the intensity of the PbS bands, while during the copper-making stage the PbO emission dominates completely. These observations seemed to indicate that, by monitoring the PbO/PbS ratio more or less continuously during the slag-making stage, one should be able to determine the correct end-point for this stage. As discussed in the introduction, this end-point determination is a crucial step in the conversion process.

The PbO/PbS ratio was followed closely during the last half-hour of the slag-making stage for a number of process cycles. A typical plot of the PbO/PbS ratio vs. time is shown in Fig. 7. The ratio is more or less constant until about ten minutes before T, i.e., the time when the operator decides to interrupt the process. During the last ten minutes, the ratio increases rapidly. In the particular cycle described in Fig. 7, the copper content of the white metal was determined to be 77.2%. This determination was made by x-ray fluorescence analysis of a white metal sample after the blow had been interrupted and cannot conveniently be performed on-line. Preliminary results show a correlation between the copper content in the melt and the PbO/PbS ratio.

Absorption. One of the main purposes of the conversion process is to remove the sulfur from the matte by the addition of oxygen. The sulfur leaves the converter in the form of SO_2, and the most straightforward way to determine the end-point of the whole converter cycle would be to monitor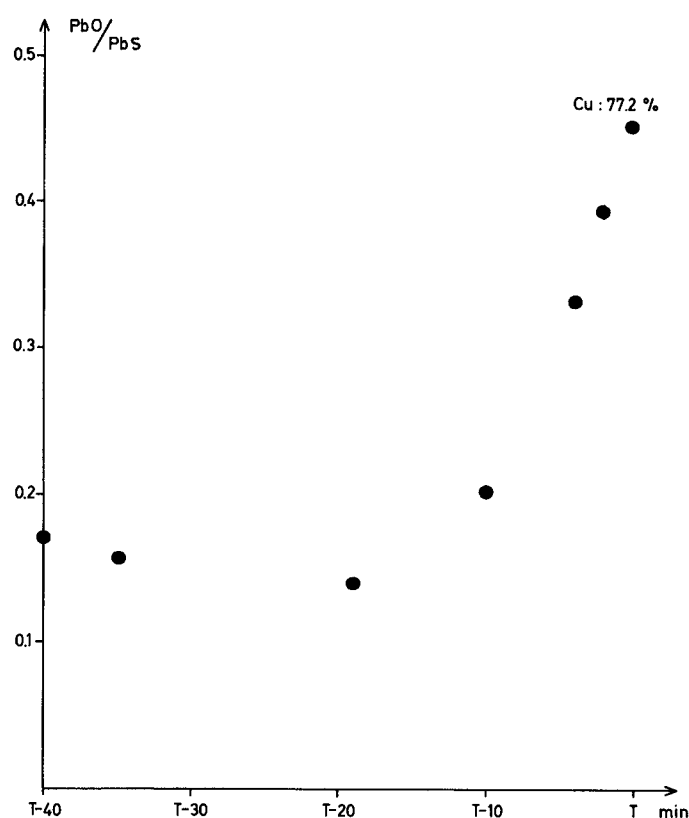 the SO_2 concentration in the process gases above the converter mouth. The SO_2 concentration remains stable at around 10 to 15% during the blasts but drops drastically when the matte becomes devoid of sulfur.

In emission, sulfur dioxide bands have been observed in the ultraviolet wavelength range in laboratory experiments.[6] However, our recordings of the emission spectra of the converter flame showed no sign of SO_2 bands, the likely reason for this observation being complete self-absorption due to the high concentration and thick layers of SO_2 above the converter.

Sulfur dioxide is known to absorb strongly in the ultraviolet wavelength range around 3000 Å. The absorption spectra of SO_2 have been used by Salomaa and Byckling[7] for the purpose of performing temperature measurements in large industrial furnaces for metal processing. Our study of the SO_2 spectrum has so far been aimed at determining the correct end-point for the copper-making stage.

The absorption measurements on the converter flame were preceded by laboratory studies. Spectra of SO_2 were obtained at different temperatures with the use of the same equipment as described earlier. A 100-mm-long quartz cell containing sulfur dioxide at 200 Torr was placed in a heat pipe (Leybold-Heraeus), and the temperature of the cell was recorded by a Chromel-Alumel thermocouple. The absorption spectrum of SO_2 at a given temperature was obtained by dividing the spectrum registered with SO_2 in the cell by a spectrum registered with an empty cell (i.e., essentially the emission spectrum of the Xe lamp). In Fig. 8 the absorption spectrum of SO_2 at three different temperatures can be seen. At elevated
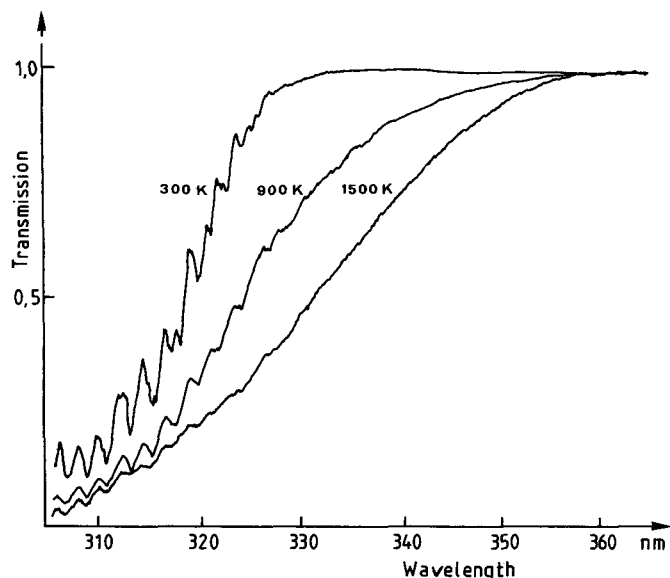
FIG. 8. The absorption spectrum of SO_2 at different temperatures. A 100-mm-long absorption cell containing SO_2 at 200 Torr was used.

temperatures the structure disappears and the absorption extends to longer wavelengths.

Absorption measurements on the converter flame were performed only during the copper stage, as the very high concentration of particles in the flame during the slag stage caused almost complete attenuation of the light from the Xe lamp. Light was transmitted through the flame, collected by the fiber coupler, and transmitted to the spectrograph through the optical fiber. The recorded light level was strongly dependent on the alignment of the optical components, which was difficult to maintain due to the harsh environment. The light level generally permitted short integration times, as described earlier. Measurements were performed with the use of different dispersions. The low-dispersion recordings essentially showed the SO_2 absorption edge around 360 nm, while the high-resolution recordings were aimed at the detection of atomic absorption. The spectra were calibrated in the way previously described.

The absorption edge of SO_2 was recorded at short intervals throughout the blow. In the beginning, the edge was positioned at about 380 nm, due to the very high concentration (10–15%) of SO_2. No light was observed below 380 nm due to the strong absorption of the gas. During the blast, the absorption edge moves towards shorter wavelengths as the SO_2 concentration drops. At the end of the blow, the edge is positioned around 320 nm. Figure 9 shows how the absorption spectrum changes during a copper blow. The end-point of this stage is critical to ±30 s, and one way to determine the end-point could be to measure the ratio of the intensities at 320 nm and 350 nm. This ratio would be zero at the beginning of the blow and increase as the end-point is reached.

CONCLUSIONS

This study has shown that emission spectroscopy can be used to characterize a copper converting process. The
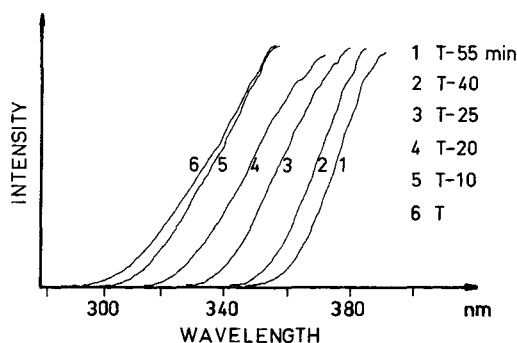

FIG. 9. The absorption of SO_2 at different times during the copper stage.

possibility of on-line measurements and data processing points towards a considerable potential for improved steering and process control, with implications for impurity elimination and correct end-point determination of the slag stage. Further measurements will be aimed at establishing the relation between the measured PbO/PbS ratio and the copper content in the melt.[8]

The implications of absorption spectroscopy for process control and minority species detection must be further investigated. However, the tentative results of the measurements during the copper stage indicate a possible method of determining the critical end-point of this stage. Measurements using higher resolution than is available at present may reveal atomic absorption by minority species, which are of considerable interest for impurity control.

For many different reasons, information about the temperature of the melt is very important for the copper converting process. This information is inherent in the spectroscopic data, and future investigations will focus on the possibility of real-time absolute and relative temperature determination.

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