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ART. XXVIII.—*On the Examination of the Bessemer Flame with Colored Glasses and with the Spectroscope;* by J. M. SILLIMAN, M.E., Adj. Prof. of Metallurgy, Lafayette College, Easton, Pa.

[Read at the Troy Meeting of the Am. Association for the Advancement of Science.]

I. *Examination with Colored Glasses.*

IN the Bessemer process, the progress of the decarbonization is determined chiefly by the appearance of the smoke, flame and sparks which are emitted from the apparatus. Owing to the rapidity with which the reactions take place, it is highly important to catch the exact moment when the blast should be turned off. This is indicated by the color and brightness of the stream of gas issuing from the converter, and by this the moment of total decarbonization can generally be accurately determined by the naked eye. When, however, pig-iron of certain qualities is used (manganiferous iron, for example) this determination is very difficult; even those who have had much experience make frequent mistakes and find it impossible to produce the same quality of steel at every blow.

In order to intensify these flame-indications, use has been made of the spectroscope, and also of various combinations of colored glasses. The former was first attempted by Dr. Roscoe, and the latter by Mr. Rowan at the Atlas Works.

Mr. Rowan experimented with a great variety of colored glasses and obtained the best results by using three glasses, two of ultramarine blue and one of dark yellow. This little instrument, or chromopyrometer, as he terms it, is now in daily use at the Atlas Works, its indications being so marked and unmistakable as to render its use safe in the most inexperienced hands.

The following experiments were made at the Bessemer Steel Works of John A. Griswold & Co., in Troy, while pursuing the chemical course in the Winslow Laboratory of the Rensselaer Polytechnic Institute. In my observations on the flame I made use of the spectroscope, and also of a combination of colored glasses. This combination consisted of two light-yellow glasses and a blue one, through which the sunlight appeared of a deep purplish-blue tint; and as it differed slightly from Rowan's, it gave somewhat different results.

In order to reproduce the appearance of the flame at the different stages of the process, I prepared a plate consisting of about a hundred varieties of colors and tints, all of which were numbered and thus referred to a table which indicated their composition. They were also arranged to be seen with either a light or dark background. The use of this plate was of necessity limited to daylight, but the illustration and description are given as occurring at night in order to show its illuminating power.

At the beginning of the process that which issues from the converter does not appear to be a true flame, but only an illumined stream of gas carrying with it innumerable red-hot pellets of iron. This gas has scarcely any illuminating power, extends but a short distance from the mouth of the converter, and is sometimes sheathed with a whitish smoke. Seen through the glasses the flame and sparks have a deep crimson color, the converter is invisible, and at the base of the flame is a crimson band which continues throughout the process.

As the reaction continues, this stream of gas grows brighter and more elongated, and after a few minutes a small pointed whitish flame appears, which suddenly increases in size. At this instant the blast-pressure falls from twenty to eighteen pounds.

When viewed through the glasses the upper part of the converter comes dimly into view, and the flame and pellets of iron appear of a lighter color, while the fragments of slag which begin to be thrown out are of a deep red. This difference in shade between the iron and slag thrown out is probably entirely owing to the lower temperature of the latter, for the reason that while the iron is discharged from the metallic bath the slag is washed up on the sides of the converter, and can be seen clinging around its mouth in a spongy mass until detached and thrown out by the blast. The greater porosity of the slag and its consequent more rapid cooling would also cause a difference of temperature.

In the second period the discharge of slag increases, and the flame is very bright and illuminating, with occasional dark streaks. Through the glasses at the beginning of this period the flame is of an ashy blue color with streaks and flashes of crimson; the edges being sometimes of a purplish hue. At this point surrounding objects are illuminated, and the converter becomes distinctly visible. A wreath of crimson is seen surrounding the flame where it strikes the chimney. By the middle of this period the crimson almost entirely disappears from the body of the flame, leaving only a slight cone at its base, and a border of greenish hue makes its appearance, and gradually grows more decided. Streaks of a dark blue color are also seen in the body of the flame.

The beginning of the third period is scarcely indicated to the naked eye, though the flame becomes somewhat weakened, and after a few minutes shows dark streaks running through it. Through the glasses at the commencement of this period the rose-colored cone begins to expand and deepen, the greenish sheath is more decided, while streaks of dark and green are visible. After a few minutes the change becomes very rapid, a few seconds only being required to reduce the flame from rose-color to the deep crimson non-illuminating gas, as at first, and again the converter is lost to view, by which time the blast should have been turned off.

The gradual fading of the crimson from the beginning of the blow and its deepening at the termination of the process, as well as the crimson band at the base of the flame and the wreath of crimson surrounding the flame at the chimney, tend to confirm Mr. Rowan's views, which are, that the different shades of crimson are due to changes of temperature. The stream of gas which comes from the mouth of the converter at the beginning of the process being illumined from within, derives its color from the metallic bath, the temperature of which, owing to the combustion of silicon, increases more rapidly during this period than at any other.

The crimson band at the base of the flame and the wreath of crimson at the chimney might also be accounted for by this theory. The flame rushing from the mouth of the converter has a tendency to create a vacuum at its base around the converter's edge, and thus to cause a wreath of flame to pass over this surface and by consequent cooling produce the crimson band. The wreath of crimson at the chimney may be also due to the cooling of the flame consequent upon deflection.

It is true we have a seeming contradiction to this theory in the rose-colored cone extending from the base at the center, which we would naturally consider the hottest part of the flame; but, as in the flame of the Bunsen burner, the hottest part is in its outer sheath, the conditions of combustion in both being similar, it is probable that that part of the flame occupied by the cone is at a lower temperature than that surrounding it.

The green streaks in the flame are most intense when the manganese spectrum is brightest; and as the color of the flame when the spiegeleisen is added is also green, we are led to suppose them due to the presence of manganese.

On two occasions simultaneous observations were made with the spectroscope and the colored glasses; but with the exception of that just mentioned, and the changes at the commencement and termination of the blow, no striking coincidence was noticed.

II. *Examination with the Spectroscope.*

The science of spectrum analysis is yet in its infancy, and there has been no scientific investigation, perhaps, which has been more contradictory in its results than that of the Bessemer flame. The first application of the spectroscope to the analysis of the Bessemer flame was made in 1862 by Dr. Roscoe at the works of Messrs. John Brown & Co., in Sheffield. Soon after this it was in constant use in Brown's works for controlling the process. It was next introduced at Crewe, and from there said to have been taken to Seraing, in Belgium, in 1865.

Roscoe's account of the general appearance of the spectrum has not altogether been verified by subsequent observers. His not having seen any line beyond 80° indicates an imperfection in his instrument. He, also, is the only one who claims to have seen the sodium line as an absorption band, or who professes to have detected the lines of nitrogen and hydrogen in the Bessemer spectrum. His spectroscope was so arranged that the spectrum of the Bessemer flame was seen in the upper half of the field of view, while the spectrum with which it was to be compared was seen immediately below. The spectrum of the flame was thus compared with the following spectra:—

1. Spectrum of electric discharge in carbonic oxyd vacuum.
2. “ “ strong spark between silver poles in air.
3. “ “ “ “ “ iron “ “ “
4. “ “ “ “ “ “ “ “ hydrogen.
5. Solar spectrum.
6. Carbon spectrum—oxyhydrogen blowpipe supplied with olefiant gas and oxygen.

The coincidences observed were very few, and totally failed to explain the value of the Bessemer spectrum. The lines of the well-known carbon spectrum did not occur at all, either as bright lines or absorption bands, nor was any coincidence observed between the lines of the Bessemer spectrum and those of the carbonic oxyd vacuum tube. The lines of lithium, sodium and potassium were strongly marked and identified with certainty. He found that three fine, bright lines between E and *b*, shown on the plate at 66½°, 67°, 67½°, coincided with those of iron; and in place of the red hydrogen line C, he discovered a black band which he considered an absorption-band, and states that it is better defined in wet than in dry weather.

In Austria, Prof. Lielegg followed up this subject with great perseverance, and gave more extended accounts of the varying character of the Bessemer spectrum during the different stages of the process. His experiments were made at Gratz, where the spectroscope was afterward used with great success in controlling the Bessemer process; but at Königshütte, where dark gray manganiferous iron was used, it was found that the indications which in other works so plainly determined the moment of decarbonization were unreliable. In this case, the lines whose disappearance is to indicate the exact point of time for ending the process, disappear too soon. During the period in which the spectrum is brightest, among the glowing vapors and gases that stream from the converter, carbonic oxyd next to nitrogen is most abundant, and it is for this reason that the first investigator, Roscoe, expressed himself as confident that the numerous lines of the spectrum were caused by this gas, although he could obtain no coincidence.

Brunner* states that "no part of the Bessemer spectrum is ever visible in the flame when the converter is heated for the first time after being re-lined, but that when the lining is not new, Lielegg's group of green lines (COγ) appears in the spectrum, which then contains also the lines of potassium, sodium, and lithium." From which he concludes that this spectrum is not to be identified with carbonic oxyd, but must be produced by other constituents of pig-iron. Others state that the Bessemer spectrum is sometimes visible while the converter is being heated after a blow. I made an observation of the flame from the converter while it was being heated the first time after being re-lined, and obtained with great distinctness the potassium, lithium, and sodium lines, but have not under any circumstances detected any other lines while the converter was being reheated.

Lichtenfels, by a series of simultaneous comparisons of the manganese with the Bessemer spectrum found the lines in the blue and green fields to completely harmonize in the two spectra. The violet manganese line which had been seen by some he could not detect in either of the spectra. I have never observed it, but Dr. Wedding, who has summed up the observations of others, states that he has repeatedly seen it. Its position is at 135½°.

The instrument used in my investigations was constructed by Alvan Clark of Cambridge, and consists of an equiangular flint-glass prism, in a metallic box, into the sides of which at the requisite angles are screwed an inverting telescope with a

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* Van Nostrand's Eclectic Eng. Mag., vol. i, page 508.

magnifying power of six, and a tube containing the adjustable slit and lens for rendering the rays parallel; also a tube with a scale, which is placed at such an angle that it is reflected from the surface of the prism through the telescope to the eye; it can be so adjusted as to appear along the upper edge of the spectrum. I was provided with Bunsen's plates of spectra on a large scale, and in order to adapt them to the scale in my instrument, I took the spectrum of the sun and obtained Fraunhofer's lines with great distinctness. Two characteristic lines in the solar spectrum were then noted, one of which appeared at 37° and the other at 117°, and a space measured equal to their distance apart as given on Bunsen's scale. This was divided into eighty equal parts, and the division extended in both directions. By the application of this scale to Bunsen's, I found that the remainder of Fraunhofer's lines in my instrument exactly coincided with their position on his plates. The correctness of the new scale was also proved by other coincidences. By moving the prism, Fraunhofer's lines will vary slightly in their relative distances apart, but in no possible position in which I could place the prism could I obtain the sun-spectrum as given by Wedding in connection with the Bessemer spectrum; if the spectrum given by him was obtained by the use of bisulphid of carbon in his prism, that substance causes a greater variation than I had supposed.

I have recorded the results of twenty-five observations on the Bessemer flame, most of which were taken at a distance of about thirty feet from the flame, though I have stationed myself at intermediate points between that and the flame; at one time sitting so close as to be almost scorched. Nearly all my observations were made at night and the lines obtained much better defined than when seen in diffused sunlight.

The record of my observations was kept as follows:—Five columns were ruled, headed—

Degree.	Color.	Brightness.	Time.	Remarks.

Note was made of the dark bands as well as the bright ones, both of which were classed according to their distinctness, as very bright, bright, faint, and very faint. In the time-column was noted the number of minutes after the commencement of the blow at which the lines appear.

At the first two or three observations I attempted to make a thorough note of the changes as they occurred throughout the whole spectrum, but afterward abandoned it as utterly impossible, as at the beginning of the second period, the lines come in so fast and the changes are so rapid that they can not be accurately noted at the exact moment of their occurrence. I therefore confined myself to a few degrees at each observation, and by this method was enabled to note accurately, and at the exact moment of their occurrence slight changes which otherwise might have escaped notice. Note was also taken of the changes in the general appearance of the whole spectrum during the successive stages of the process. After having made half a dozen observations, while viewing the spectrum of the flame from the converter while it was being heated for another charge, it was discovered that a movement of the eye before the eye-glass occasioned a similar movement of the lines of the spectrum along the scale, on which their position could thus be made to differ more than half a degree. I have seen no notice of this in the statements of others, and it may account for some of the apparent discrepancies. Thereafter, when taking the readings of any of the lines, the position of the eye was so adjusted as to bring the sodium line exactly at 50°. Owing to the extreme brilliancy of the flame the aperture may be made exceedingly narrow, and thus the many lines of the spectrum which with a duller light and broader gauge would be blended together, may be separated.

At the beginning of the blow, the spectrum is continuous and very faint, and generally extends from 35° to 120°, covering about three-fourths of the length attained in the second period. This increases slightly in extent and brightness until the appearance of the sodium line. This line appears at the end of the first period at the beginning of a more decided flame. It comes flashing through from one extremity to the other for an instant, and then disappears only to return the next instant in brighter flashes which are continued for about a minute, by which time the line becomes permanently established. On one occasion the sodium line, instead of flashing and disappearing as usual, continued visible after a few seconds, and expanded and contracted in width almost isochronously until it became permanently established. The appearance of this line indicates the termination of the first period. This period I have found to vary in extent from three to seventeen minutes in blows lasting from thirteen to twenty-seven minutes. None of the other lines make their appearance in vivid flashes as does the sodium. The lithium line becomes visible three or four minutes after the first flash of the sodium. It is very faint at first but soon becomes quite distinct and lasts through the blow. The vivid flashing of the sodium line may be accounted for by the exceedingly small amount of sodium required to produce its spectrum—an amount not exceeding $\frac{1}{180000000}$ of a grain. The slightest momentary combustion taking place in the stream of gas from the converter, would at that instant render glowing a sufficient amount of the vaporized sodium to produce its spectrum, and thus occasion the flashes so characteristic in the first appearance of that line. Lithium exists in a much smaller quantity and requires $\frac{1}{6000000}$

of a grain, or thirty times that given for sodium. By the time the lithium line is established the red potassium line at 23½° and occasionally the violet line at 135° appear, and the blue and green fields become divided into bands which are so rapidly resolved into bright and dark lines, that it is difficult to note the exact time of the appearance of each. The spectrum increases to a dazzling brightness, and extends itself in both directions until it reaches from 23½° to 140°.

During the third period the spectrum becomes more brilliant, and the lines more distinct. Several new lines make their appearance in different parts of the spectrum, of which the ones at 51½°, 57°, and 67° are well defined, while others are faint and not always visible; some of them appearing only toward the close of the last period. In viewing the lines in the most refracted part of the spectrum, it has been repeatedly observed both by myself and others, that these lines were more strongly marked when entering the eye at an angle than when viewed directly. That this was not imagination is proved by repeated identification of lines at the same point on the scale.

At the termination of the blow the lines are rapidly swept away, sometimes in the inverse order of their appearance, but more generally they disappear within the space of two or three seconds, leaving a continuous spectrum as at first, though somewhat brighter. Sometimes the sodium and lithium lines are swept away with the others, and at other times they remain visible. In either case the change is very decided, and does not generally occupy more than three seconds. In the course of my observations, thirty-three lines have been detected, as given in the table below.

Some of the lines given by Lielegg I have failed to find, but have detected others not given by him.

1st Period, 23½, 35, 50, 135.
2d Period, 23½, 35, 43, 44, 44½, 45½, 46, 47½, 48½, 50, 52, 53, 56, 56½, 61½, 62, 62½, 63, 65, 66½, 67½, 70, 72, 120, 135.
3d Period, 23½, 35, 43, 44, 44½, 45½, 46, 47½, 48½, 50, 51½, 52, 53, 56, 56½, 57, 61½, 62, 62½, 63, 65, 66½, 67, 67½, 70, 72, 100, 102, 103, 105, 108, 135.

Among the dark bands detected, the most intense occurred at 44–46, 51–55, 56–58, 62–64½; others were found at 33–34½, 36½, 37½, 38½, 40, 68–72.

Many of the dark bands were crossed by bright lines.

I have repeatedly observed the dark band considered by Roscoe to be a hydrogen absorption line, but have not noticed that its intensity varied with the dampness of the weather. Whether it is an absorption band or not can be determined by a series of observations continued through wet and dry weather. If this proves to be a hydrogen line, the Bessemer spectrum will be found more complicated than is generally supposed. It has been thought by some that the dark bands in the spectrum are absorption lines due to the cooling of the outer sheath of flame, but it is more probable, that although the pellets of iron and slag tend to produce a faint continuous spectrum; yet in contrast with the very brilliant lines it appears discontinuous, the dark bands being merely intervals between the bright ones. The iron spectrum has not been satisfactorily identified. It has been suggested that the brightness and size of the lines of the Bessemer spectrum do not allow the iron lines to appear. In comparing the Bessemer spectrum with Bunsen's spectra of nickel, cobalt and calcium, no coincidences were observed except two or three in the latter spectrum. The brightest calcium line, however, was not visible in the Bessemer spectrum. The Bessemer spectrum contains yet many mysteries to be solved, among which is the cause of the non-appearance of the lines of the spectrum at the beginning and termination of the blow.

This was readily solved when the numerous lines of the spectrum were attributed to carbon, but in proving them to be caused principally by manganese, their disappearance is not so readily accounted for.

One theory to account for it is that the luminous power of the flame is too small at the beginning and end of the process to produce a spectrum. In regard to this it may readily be shown that the brilliancy of the spectra of incandescent metallic vapors does not depend upon the illuminating power of a flame but upon the heat of the flame into which they are introduced. For instance, the spectra are more distinct in the non-luminous flame of a Bunsen lamp than in the ordinary luminous gas-flame. If we take the theory as referring to the feebleness of light given off by those substances in the flame which produce the spectrum, it will resolve itself into the one of change of temperature, notwithstanding the fact that the illuminating power of flames of the same temperature varies with the composition of the gas, because there is evidently enough sodium in the flame to give its characteristic line; hence, whatever might be the illuminating power of the flame, if the heat is sufficiently intense the sodium line *will* show itself.

Dr. Wedding adopts the theory that the absence of the spectrum at the beginning and termination of the blow is because the absolute quantity of the bodies volatilized producing the spectrum is at these times too small. His reasons for holding this view are as follows:—"A trace of sodium will give its characteristic line, but, according to Simmler, a much larger quantity of manganese is needed to obtain a recognizable reaction than that which can be detected by the well known blow-pipe reaction with carbonate of soda. Consequently, spectrum analysis does not depend alone upon the *presence* of a body but also upon the presence of a certain quantity. And although manganese is always left in the iron, it may not be left in sufficient quantity at the termination of the blow to produce the spectrum, and for this reason the lines disappear."

To this theory there are same some strong objections. 1*st.* If we take manganese in sufficient quantity and hold it in a flame the spectrum will increase in brightness until a uniform temperature is attained; but when the amount of manganese vaporized begins to diminish, its spectrum will gradually decrease in brightness until it disappears. Now, if the disappearance of the manganese lines in the Bessemer spectrum is owing to the diminution of the quantity of manganese, we should infer that these lines would gradually grow more indistinct and then fade away; but on the contrary, the manganese spectrum increases in brilliancy from its first appearance, and is more intense just before being swept away than at any other time. The analysis of the smoke, which appears when the flame ceases, proves that a considerable quantity is still volatilized, and it is notable that in manganiferous iron this quantity increases towards the close of the blow. 2*nd.* It would be more difficult to account by this theory for the non-appearance of the sodium line at the beginning of the blow, as sodium then in all probability exists in the issuing gas in sufficient quantity to produce its spectrum at a high temperature, as it is only by special precaution that we can keep it out from any flame. 3*rd.* A still greater difficulty would arise in applying this theory to the spectra of sodium and lithium at the close of the blow. As has before been stated, these lines sometimes disappear at the moment of complete decarbonization, and sometimes remain. In the former case, to say that our friend sodium had given out would be doing great injustice to that element, as it has never given us reason for bringing so grave a charge against it. Dr. Wedding in attempting to demonstrate that the non-appearance of the manganese lines is owing to the lack of sufficient quantity volatilized to produce its spectrum, makes the following statements:—

From analyses made by Brunner we find that the manganese contained in the iron falls from 3·460 per cent in the raw material, to 1·645, 0·429, and finally to 0·113 per cent in the decarbonized product; and that the protoxyd of manganese in the slag first increases from 37·00 per cent to 37·90 per cent, and then sinks to 32·23 per cent, and furthermore, that a certain quantity of manganese is to be found in the smoke. How much manganese is really lost by volatilization cannot be determined, since data are wanting as to the absolute quantity of slag and iron, consequently we cannot determine how much manganese has been lost by means of the eruptions.

But since the manganese contained in the pig-iron decreases constantly, and that contained in the slag after the termination of the boiling period also decreases, a considerable volatilization of this body is probable just at the time when the spectrum is best developed. Comparing with this the experiments that can be made in the laboratory we arrive at the hypothesis, that the oxydized manganese which has entered into the slag is not volatilized but is retained by the slag; it can, therefore, get into the flame only in the shape of solid or fluid combinations.

In the above statements the results of the analysis prove that some of the manganese in the slag is volatilized. We cannot consider the manganese spectrum during the entire process as due wholly to the volatilization of the manganese directly from the iron, for while the amount eliminated from the iron grows continually less, the manganese spectrum grows brighter. Owing to the intimate mixture by the blast of the iron and slag, the manganese oxyd contained in the latter, is brought in contact with the melted iron and vaporized. This mixing of the slag and iron would cease at the termination of the process, and this would account for the sudden diminution of smoke.

If there was a sufficient carbonic oxyd flame to render the escaping gases glowing it is evident they would not issue from the converter as dark smoke, but as incandescent vapor having its characteristic spectrum. The lack of sufficient flame may, therefore, account for the disappearance of the manganese spectrum. The Bessemer flame presents other problems, and opens an intensely interesting field for scientific investigation; and by the use of more delicate instruments than have yet been employed for this purpose, discoveries may be made which will throw new light upon the subject of spectrum analysis.