THE EMISSIVITY OF METALS AND OXIDES

IV. IRON OXIDE

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I. INTRODUCTION

The present paper is a continuation of the study of the radiometric properties of metals and oxides. The experimental methods and bibliography of the subject have been given in the preceding three numbers of the series.[1]

The object of this investigation has been the determination of the monochromatic emissivity for a wave length $\lambda = 0.65\mu$ and the total emissivity of the oxide of iron formed by heating iron in air.

The oxide thus formed is usually considered to be magnetite, but Messrs. Sosman and Hostetter,[2] of the Geophysical Laboratory, have found that actually it may be almost any combination of FeO and Fe_2O_3. This fact may account in part for slight changes observed in the radiometric properties of the oxide surface.

In the present investigation the iron upon which the oxide formed contained about 0.12 per cent carbon. The following is a report upon the analysis of several samples of the oxide by J. R. Cain, of this Bureau:

These oxides are magnetic and free from metallic iron (as shown by test with copper salt). Hence they are of the magnetite type. However, the material is not pure Fe_3O_4, inasmuch as the gain in weight on heating in air is greater than would correspond to the reaction: $2Fe_3O_4 + O = 3Fe_2O_3$, which represent the change normally taking place when magnetite is heated in air. There is, therefore, a large proportion of ferrous oxide, FeO. Assuming that only FeO and Fe_3O_4 are present, the composition

[1] Burgess and Foote, Bureau Standards Scientific Paper No. 224; Burgess and Waltenberg, Bureau of Standards Scientific Paper No. 242; Foote, Bureau of Standards Scientific Paper No. 243.
[2] The published paper will appear shortly.

may be calculated to be approximately 60 per cent FeO and 40 per cent Fe_3O_4. The radiating surface is not a single substance; at least FeO and Fe_3O_4 are present, and possibly solid solutions or compounds of these, with the possibility of existence of Fe_2O_3 on the surface directly exposed to air and of allotropic forms of the oxides or compounds within the investigated temperature range.

Iron oxide has proven an especially difficult material with which to obtain satisfactory measurements, on account of scaling and flaking from the iron surface upon which the oxide is formed. This oxide is extremely brittle and does not form in a tough thin coat, as in the case of the nickel oxide NiO. The latter oxide presents a smooth surface, showing some luster, while iron oxide is silky in appearance and pitted with minute depressions; its surface is entirely without luster—almost a dead matt. For this reason the emissivity is very high, the small depressions or granular structure producing the effect of a collection of minute black bodies. If a microscopic sample of the oxide is melted upon a platinum strip [3] and cooled below the melting point, the surface is then bright and smooth, similar to that of a polished crystal of magnetite. In this case the emissivity is much less. This type of surface, however, does not occur in general practice, and hence it was thought desirable to determine the correction necessary to apply to readings of optical and radiation pyrometers when sighted upon the type of surface of the oxide formed upon iron heated in the open. These corrections may therefore be used in technical practice when the temperatures of rails, ingots, etc., are measured radiometrically.

II. MONOCHROMATIC EMISSIVITY ($\lambda=0.65\mu$)

A number of different methods were tried in the determination of the monochromatic emissivity. Iron tubes of various sizes and iron wedges did not prove satisfactory on account of the large temperature gradient through the oxide, flaking, and temperature variation of the surface. Measurements with the spectrophotometer, employed in a preceding paper, were not reliable. The only method which gave satisfactory quantitative results was that of the microscopic melts.[4] A small sample of the oxide

[3] Burgess and Waltenberg, Bureau of Standards Scientific Paper No. 242.
[4] Burgess and Foote, Bureau of Standards Scientific Paper No. 224, p. 42.

formed by heating iron strips in air was flaked off and placed on a nickel or platinum strip heated electrically. Upon the oxide were placed minute samples of sodium chloride, sodium sulphate, and gold. The current through the heating strip was gradually increased until the standard sample melted, when at the instant of the melting the apparent temperature of the oxide surface was observed by a Holborn-Kurlbaum optical pyrometer, using light of wave length $\lambda = 0.65\mu$. The results are summarized in the following table:

TABLE 1

Emissivity of Iron Oxide by Microscopic Melts ($\lambda = 0.65\mu$)

Observations	Material	True temperature, ° C	Observed temperature, ° C.	Average deviation from mean	Emissivity observed
9	NaCl	801±1	801	±1.5	1.00
22	Na₂SO₄	884±1	882	±3	0.97
16	Au	1063±2	1058	±2	0.94

The emissivity E_λ is given by the equation:

$$\frac{1}{T} - \frac{1}{S_\lambda} = \frac{\lambda}{0.4343C_2} \cdot \log E_\lambda$$

where T is the true absolute temperature, S_λ the observed absolute temperature, λ the wave length of the light in μ and $C_2 = 14450$.

Apparently the emissivity decreases slightly with increasing temperatures, as in the case of the oxide of nickel and other oxides. In the case of nickel oxide the curve, true temperature vs. E_λ for $\lambda = 0.65\mu$, was found to be a straight line in the range 800 to 1300° C. If it is permissible to extrapolate similarly the values obtained for iron oxide, neglecting the determination at 801° C, one obtains the following:

TABLE 2

Monochromatic Emissivity of Iron Oxide ($\lambda = 0.65 \mu$)

True temperature, °C	800	900	1000	1100	1200
Emissivity	0.98	0.97	0.95	0.93	0.92

Obviously the values given above are questionable, but a large error in emissivity will make very little difference for these high emissivities in the corrections necessary to apply to the readings of an optical pyrometer. (See Sec. IV.)

III. TOTAL EMISSIVITY

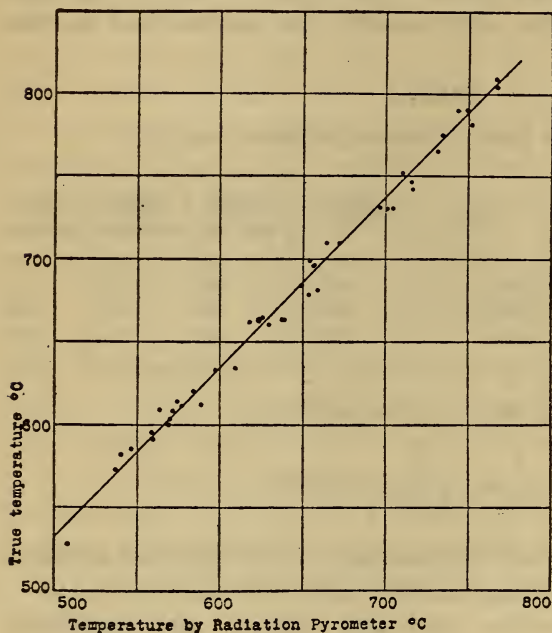The total emissivity was determined by means of a Féry pyrometer, as in a preceding paper.[5] Iron tubes of different sizes were heated electrically in air; the apparent temperature of the oxide surface was measured by the radiation pyrometer and the true temperature was obtained by the corrected readings (Table IV) of the optical pyrometer. Fig. 1 represents the observations graphically.

FIG. 1.—Temperature of iron oxide by radiation pyrometer versus true temperature

The relation between true, T, and apparent, S, absolute temperatures and the total emissivity, E, is as follows: $E = (S/T)^4$. The following values are thus obtained from the data in Fig. 1.

TABLE 3

Total Emissivity of Iron Oxide

True temperature, °C	500	600	700	800	900	1000	1100	1200
Total emissivity	0.85	0.85	0.86	0.87	0.87	0.88	0.88	0.89

It was not possible to carry the actual observations further than from 500 to 800 ° C on account of temperature variations over the surface of the oxide, but in view of the fact that the general course

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[5] Burgess and Foote, Bureau of Standards Scientific Paper No. 224, p. 55.

of the total emissivity curves of metals and oxides is fairly definitely established both theoretically and experimentally [6] it seems permissible to extrapolate the above data to 1200 ° C.

IV. CORRECTIONS TO THE READINGS OF OPTICAL AND RADIATION PYROMETERS

The following table gives the relation between the true temperature of an iron oxide surface and the apparent temperature measured by an optical and by a radiation pyrometer:

TABLE 4

Optical ($\lambda=0.65\ \mu$) and Radiation Pyrometers Sighted on Iron Oxide

Observed temperature, °C	True temperature	
	Optical pyrometer, °C	Radiation pyrometer, °C
500	....	530
600	600	630
700	700	735
800	801	835
900	902	940
1000	1004	1040
1100	1106	1145
1200	1210	....

V. TEMPERATURE GRADIENT THROUGH THE OXIDE

A large temperature gradient was observed to exist through the oxide layer formed on the surface of iron tubes heated electrically in air. In Fig. 2 are given the observations of the true temperature of the outside of the oxide and the temperatures of the iron tube immediately under the oxide. The latter temperatures were determined by means of a thermocouple inside the tube, the temperature gradient through the iron itself being found negligible.

Apparently this temperature drop through the oxide is qualitatively, at least, independent of the size of the tube, several different sizes being employed. The thickness of the oxide is automatically rendered approximately of the same order of magnitude for

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[6] Aschkinass, Ann. d. Physik (4), **17**, p. 960; 1905. Foote, Bureau of Standards Scientific Paper No. 243. Burgess and Foote, Bureau of Standards Scientific Paper No. 224. Langmuir, Trans. Am. Electrochem. Soc. **23**, pp. 299–332; 1913. Randolph and Overholser, Phys. R. (2), **2**, pp. 144–152; 1913.

different times of heating or for different sized tubes by flaking and dropping off. The values represented by crosses were taken from the work of Burgess, Crowe, Rawdon, and Waltenberg[7] upon a section of a 100-pound rail cooling in the open. In this case the
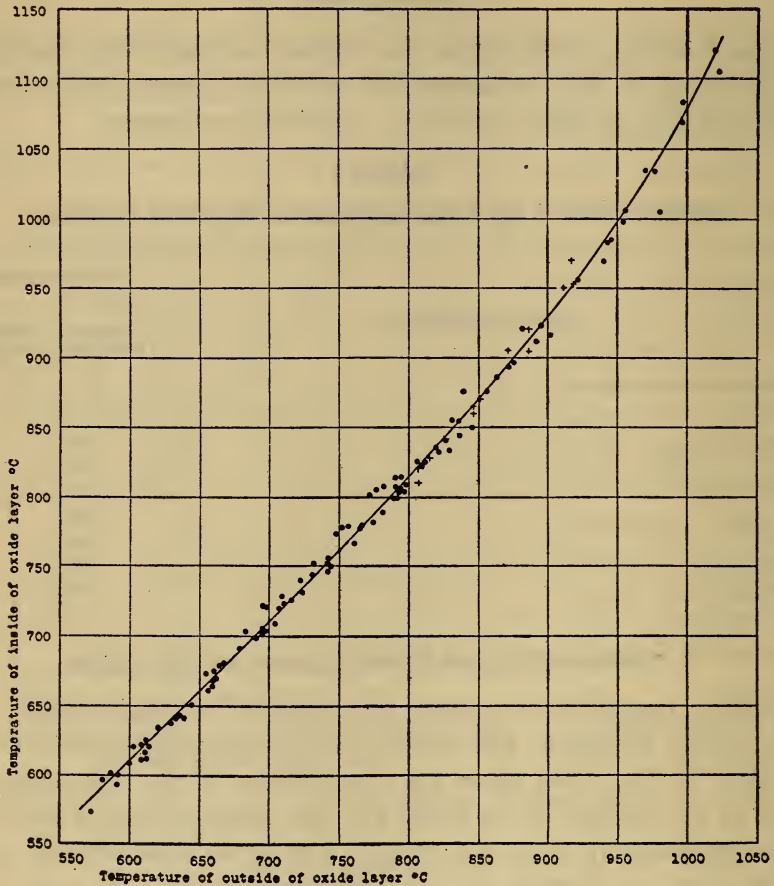

FIG. 2.—Temperature of outside of iron oxide layer versus temperature of inside of oxide layer

temperature under the oxide was determined by a thermocouple inserted in a small hole drilled parallel to the length of the rail and as near the outside as possible. The outside temperature of the oxide was measured by an optical pyrometer. It is therefore

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[7] Burgess, Crowe, Rawdon, and Waltenberg, Bureau of Standards Technological Paper No. 38.

evident from a consideration of Fig. 2 that the temperature of the outside of the iron oxide is considerably less than that of the iron surface underneath.

The large temperature drop from the metal surface to the outside of the oxide is due in part to the low thermal conductivity of the oxide and in part to what appears to be an actual air gap between the metal and the oxide caused by the peeling away of the oxide from the metal upon which it is formed.

VI. CONCLUSION

The monochromatic emissivity ($\lambda = 0.65\mu$) and the total emissivity of iron oxide formed by heating iron in air have been measured with an accuracy which is rather unsatisfactory, but which appears to be about as good as can be obtained when one considers the variable character of the surface, the constant scaling and flaking, and temperature variations occasioned by this flaking.

Iron oxide in the spectral region ($\lambda = 0.65\mu$) is almost "black," having an emissivity varying from 0.98 to 0.92 in the range 800 to 1200° C. The corrections necessary to apply to the readings of an optical pyrometer in this temperature range vary from 0 to 10° C. The total emissivity of iron oxide increases from 0.85 at 500° C to 0.89 at 1200° C. The corrections necessary to apply to the readings of a radiation pyrometer in this temperature range vary from 30 to 50° C.

The temperature of the outside of the oxide layer is considerably different from that of the inside in contact with the metal on account of in part the low thermal conductivity of the oxide and in part, undoubtedly, the actual separation of the outside oxide layer from the metal, thus forming an air gap between the two surfaces or between two surfaces of oxide, the outer one thick and the inner one thin. The drop in temperature through the oxide layer is approximately constant for various sized samples from small iron tubes to 100-pound rails, and increases rapidly with temperature rising to about 100° at an outside temperature of 1100° C.

WASHINGTON, March 31, 1915.