



CaF<sub>2</sub> with a water molecule

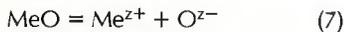


is a more important source of fluorine loss than the reaction given by Equation 5.

The basicity index given by Equation 4 has been used by the IIW and the welding industry, and referred to in this paper as the IIW index.

### Ionic Theory

Since the proposal of the ionic theory of slag-metal interactions in steel-making systems by Herasymenko and Speight (Ref. 11) followed by Flood and Forland (Ref. 12), the ionic theory of oxide melts has gained acceptance by researchers. According to the ionic theory, a basic oxide, MeO, dissociates into a metal cation and releases oxygen anions as



An acidic oxide, such as SiO<sub>2</sub>, consumes an oxygen anion as



to form a silicate anion. The above reaction equation may be depicted in a general form as (Refs. 2, 13)



where O<sup>°</sup> is the polymerized network of silicate oxyanion, O<sup>-</sup> is the depolymerized silicate anion, and O<sup>2-</sup> is the available oxygen anion. Lux (Ref. 14), Flood and Forland (Ref. 12) defined a basic oxide system as one with a high oxygen anion concentration. Froberg and Kapoor (Ref. 15) utilized the above concepts to derive a basicity index analogous to the pH scale used in aqueous solutions, and is given by

$$\text{pO} = -\log(a_{\text{O}^{2-}}) \quad (10)$$

where a<sub>O<sup>2-</sup></sub> is the activity of the oxygen anions, and pO is the potential of oxygen. Although the above expression is simple to use, two of its major drawbacks are that: 1) it was derived by applying the theory of ideal silicate mixing; and 2) it is not possible to determine the oxygen anion activity a<sub>O<sup>2-</sup></sub> (Refs. 16, 17).

### Optical Basicity

A fundamental drawback of the above expressions for a basicity index has been the neglect of the role played by cations. This problem was encountered by Wagner (Ref. 16) in determining the basicity of oxides with transition metal ions that undergo valence changes with changing oxygen anion concentration.

From research on glass systems, two chemists, Duffy and Ingram (Ref. 18), were the first to provide answers to the questions posed above. They define cations as polarizing, such as Si, Ti, ions, etc. and as nonpolarizing, such as Na, K and

Ca ions. A polarizing cation draws the negative charge away from oxygen anion, resulting in the formation of a covalent bond. The extent of covalent bond formation is dependent on the affinity of the polarizing cation for the negative charge; this affinity is estimated by Pauling's electronegativity. The degree to which the oxygen anion donates its negative charge to the cation defines the "state" of the oxygen ion. A quantitative measure of the electron donor power of the oxygen anion is defined as the Lewis basicity of the oxide system (Refs. 19, 20).

### Optical Basicity Index

Analogous to the litmus test for aqueous solutions in which a color change indicates the pH of the medium, a probe ion is added to an oxide melt or glass. The electron donor power of the oxygen ion to the probe ion is observed as a "red" shift in the UV bands of the probe ion. This is due to the expansion of the s-orbital, called the nephelauxetic effect in structural chemistry, resulting from electron donation from the oxygen anion (Ref. 18). This spectral shift, measured by Duffy and Ingram, gave an expression for a basicity scale. Since this expression was measured by a spectroscopic technique, they coined such a basicity expression as "optical" basicity (Refs. 18, 21). This is given by

$$\text{optical basicity} = \frac{\text{electron donor power of oxygen in oxide system}}{\text{electron donor power free oxide anions}} \quad (11)$$

that is (Ref. 22),

$$\text{optical basicity} = \sum_{\text{cations}} \frac{\text{all } Z_A \cdot R_A}{2 \cdot G_A} \quad (12)$$

where Z<sub>A</sub> is the coordination number of the cation A. R<sub>A</sub> is the ratio of the moles of cation A to the total moles of oxygen atoms, and G<sub>A</sub> is the basicity moderating parameter, which is a function of Pauling's electronegativity. The optical basicity expression given by Equation 12 is referred to as optical basicity index or OB index throughout this paper.

### Welding Flux Basicity

The basicity index of a welding flux is determined by using the IIW index given by Equation 4, which is derived from the theory of undissociated, molecular oxides. Despite the drawback of the nonexistence of undissociated oxides in oxide melts, the welding industry adapted Equation 4 as a measure of flux basicity. But the alternative of using the basicity index derived from the ionic theory, pO, could not be applied suc-

**Table 1—Optical Basicity Index Values of Some Oxide Systems**

Oxide System	OB Index	IIW Index
K <sub>2</sub> O	1.36	Infinity
Na <sub>2</sub> O	1.15	Infinity
CaO	1.00	Infinity
MgO	0.78	Infinity
FeO	0.51	Infinity
FeO-Fe <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	0.76	Cannot be determined
CaO-TiO <sub>2</sub> -SiO <sub>2</sub>	0.61 <sup>(a)</sup>	0.55 <sup>(a)</sup>
Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> -SiO <sub>2</sub>	0.55	0.0
Al <sub>2</sub> O <sub>3</sub>	0.59	0.0
TiO <sub>2</sub>	0.55	0.0
SiO <sub>2</sub>	0.48	0.0

(a) See appendix.

cessfully due to the uncertainty in the estimation of oxygen ion activity.

The aim of this investigation was to conduct a comparative study of the drawbacks of the IIW basicity expression given by Equation 4 with the OB index given by Equation 12. Table 1 is a listing of the basicity values of some oxides and oxide systems using the IIW and the OB indices. It is apparent that single oxide components do not have a finite basicity value using the IIW expression but have a finite value using the OB index expression. It will be shown that major drawbacks of the IIW expression are overcome by using the OB index expression.

### Experimental Procedure

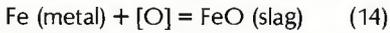
The flux cored electrode formulations chosen were T-1 and T-5 types classified under AWS A5.20. Formulations chosen were such that a wide range of basicities could be determined without adversely affecting the weldability characteristics. Samples of flux cored electrodes of 3/32-in. (2.4-mm) diameter were manufactured with the chosen formulations.

Welding was carried out using an automatic setup consisting of a Hobart Mega-Mig 450 RVS power source, Hobart Mega-Con 114-X remote feed controller and a Hobart Motoman 5-axis robot in conjunction with a Yasnac RX control system. Tensile plates were welded in accordance with the requirements of AWS Specification A5.20. Carbon dioxide shielding gas was used. All welds were made in the flat position with a fixed electrode extension of 0.75 in. (19 mm) and a travel speed of 12 ipm (305 mm/min). DCEP polarity was used at three different settings of 375 A/26 V, 420 A/29 V, and 480 A/31 V. All plates were stored at room temperature for 48 h to allow diffusible hydrogen to escape before machining.

One tensile specimen and one set of five Charpy V-notch impact specimens were machined from each plate per AWS specifications. The tensile specimens



controlled by FeO content of the flux through the reaction (Refs. 10, 23, 24).



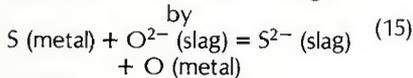
North, *et al.* (Ref. 24) maintains that any correlation between basicity and weld metal oxygen is incorrect, but Wagner (Ref. 16) supports the use of correlations in the study of basicity, and others (Refs. 25, 26) have studied the relationships between basicity and weld metal oxygen contents.

With this in view, weld metal oxygen contents were correlated with the basicity values obtained by using the IIW and the OB index expressions. Figures 1 and 2 are the plots for the IIW and OB indices against weld metal oxygen at 420 A and 29 V. For the T-1 type of flux formulations, the basicity values using the IIW index expression gave a zero or a negligibly small value as can be seen from Fig. 1. This is a result of using a base/acid ratio in estimating the basicity index for a flux that is predominantly acidic in nature. In the correlation between the IIW index and the weld metal oxygen contents, the variability was large, and the regression coefficient was 0.34. It was therefore not possible to derive a meaningful regression relationship. On the other hand, by applying the OB index expression to these flux formulations, a high linear regression coefficient of 0.82 was obtained, with a much lower variability.

The above trend was observed at other settings of 375 A/26 V, and 480 A/31 V. The oxygen values did not vary appreciably at the three parameter settings, indicating that the oxygen transfer is not a strong function of heat input used in this study.

### Basicity-Sulfur Correlations

Desulfurization reaction is given



wherein the extent of sulfur removal from the metal phase is dependent on the concentration of the oxygen anions. From iron- and steel-making processes, it is a well-known fact that a "basic" content in the slag is a prerequisite to obtain a "clean", low-sulfur metal (Ref. 3). Therefore a basic slag is one which has a high oxygen anion activity (Refs. 12, 14, 15). As mentioned earlier, the estimation of the oxygen ion activity is not possible. An alternative method of defining the basicity of the slag becomes necessary. Wagner (Ref. 16) had defined basicity in terms of sulphide, carbonate and other capacities in correlation studies involving slag-metal reactions.

In the present investigation, the IIW index and the OB index expressions were used to study the relationships between the weld metal sulfur contents and the

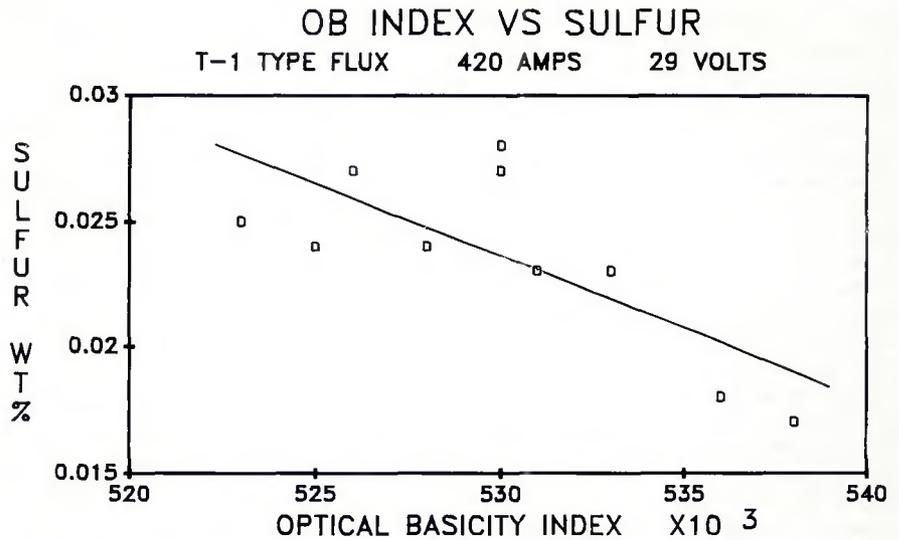


Fig. 4 - Correlation of weld-metal sulfur content with the OB index for the T-1 type of flux cored electrodes welded at 420 A and 29 V

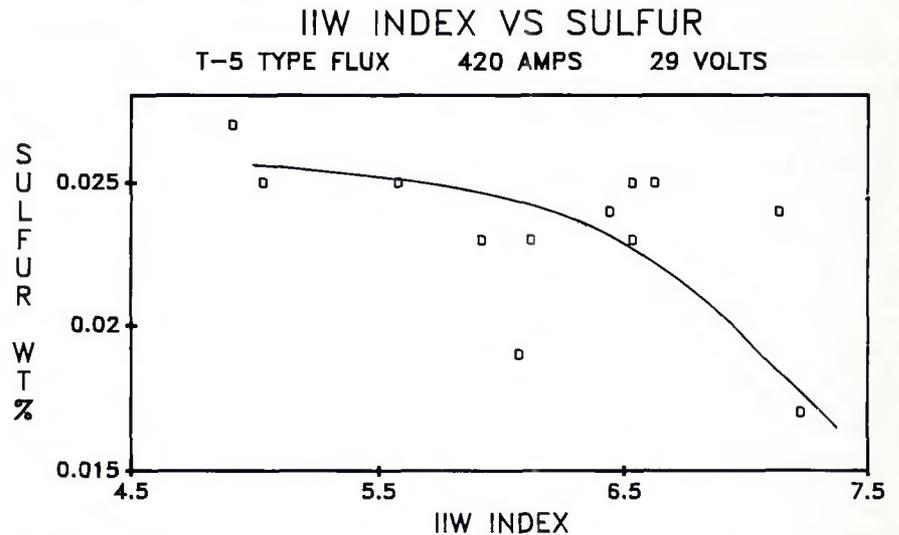


Fig. 5 - Correlation of weld-metal sulfur content with the IIW index for the T-5 type of flux cored electrodes welded at 420 A and 29 V

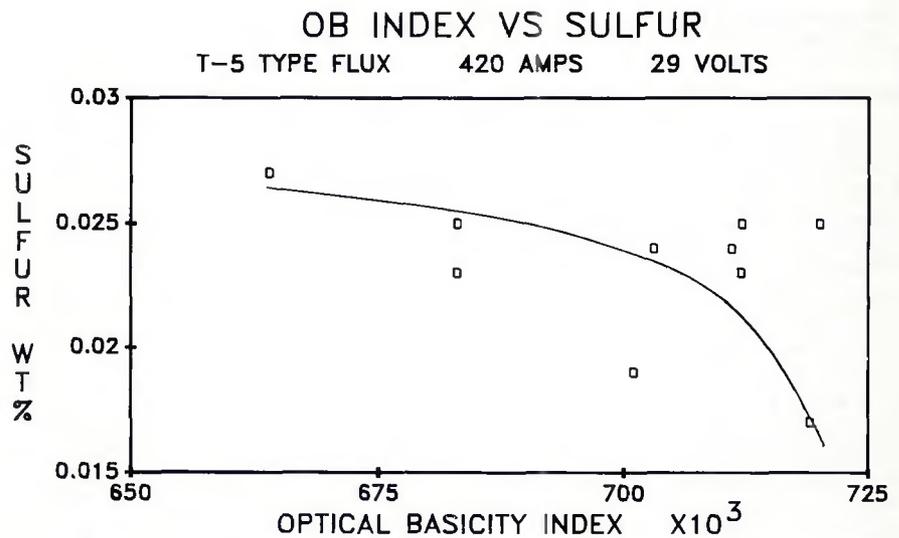


Fig. 6 - Correlation of weld-metal sulfur content with the OB index for the T-5 type of flux cored electrodes welded at 420 A and 29 V









