

Control of Diffusible Weld Metal Hydrogen through Flux Chemistry Modification

The influence of fluoride and calcite flux additions on the hydrogen content of shielded metal arc welds was examined

BY J. DU PLESSIS, M. DU TOIT, AND P. C. PISTORIUS

ABSTRACT. This project examined the feasibility of using flux modification to reduce the as-deposited hydrogen content of basic-type shielded metal arc welds. Flux formulations containing additions of fluoride-containing compounds (CaF_2 , NaF , K_2AlF_6 , and K_2TiF_6) and calcite displayed lower hydrogen levels, with the diffusible weld metal hydrogen content reaching a minimum with increasing additions. Higher levels caused an increase in the weld hydrogen content. Thermodynamic slag modeling attributes the existence of these minima to a decrease in slag water capacity with an increase in slag fluoride content (at constant basicity), brought about by higher concentrations of fluoride-containing compounds in the flux formulation. The effect of flux additions on the weld mechanical properties and the electrode operating characteristics was not evaluated during the course of this investigation.

Introduction

Despite extensive research, hydrogen-assisted cold cracking remains prevalent in higher-strength steel welds (Ref. 1). A heavy responsibility is placed on the fabricator to incorporate appropriate safeguards against hydrogen-assisted cracking in welding procedures. In addition to prescribing low-hydrogen basic-type welding consumables (treated in the recommended manner), fabricators rely on preheating, interpass temperature control, and postweld heat treatment to reduce the risk of cracking during welding. These traditional hydrogen control methods are costly and time consuming.

During shielded metal arc welding (SMAW), the preheat and interpass tem-

peratures required to prevent hydrogen-assisted cracking are a function of the hydrogen potential of the welding consumable. An incentive therefore exists for welding consumable manufacturers to reduce the hydrogen content of basic-type SMAW electrodes, and modification of the arc chemistry through the use of flux additions presents an attractive option. The development in recent years of flux systems with low baseline moisture contents and low moisture pickup rates has already reduced as-deposited weld metal hydrogen contents significantly. Welding consumable manufacturers are currently striving to produce welding consumables with increasingly lower as-deposited weld metal hydrogen contents. Current benchmarks are less than 3 mL hydrogen per 100 g of weld metal for SMAW electrodes, and less than 2 mL hydrogen per 100 g of weld metal for flux cored arc welding (FCAW) consumables.

Published literature suggests that the diffusible weld metal hydrogen content can be manipulated through arc chemistry modifications (Refs. 1–4). The majority of these investigations focused on submerged arc wire and flux systems and on flux cored wires. These systems are simplistic in the sense that the flux formulations contain a limited number of ingredients. Very little has been reported on hydrogen control through arc chemistry modifications for the more complex flux systems of SMAW electrodes.

Hydrogen Reduction Strategies

A number of theoretical models have been proposed in published literature as

possible methods of reducing weld metal hydrogen contents (Refs. 1–6). Some of these theoretical models suggest ways of reducing the diffusible hydrogen content of shielded metal arc welds through modification of the electrode coating formulation. A brief overview of the hydrogen reduction strategies relevant to this investigation follows.

Increasing the Slag Basicity

Slag basicity is related to the ease with which oxides dissociate into cations and oxygen anions (Ref. 7). Oxides that dissociate readily are termed “basic” and those that only partially dissociate are termed “acidic.” A high-basicity slag is therefore considered to have a high concentration or high activity of free oxygen ions, O^{2-} . The basicity index of flux is usually calculated by dividing the total weight-percent-age of basic flux components by the sum of the acidic and amphoteric components, as shown in Equation 1.

$$\text{Basicity} = \frac{\sum \text{Basic oxides}}{\sum \text{Acidic and amphoteric oxides}} \quad (1)$$

Numerous basicity indexes for fluxes have been derived to date. The most commonly used empirical basicity index, developed by Tulliani et al. (Ref. 8), is shown in Equation 2.

$$\text{Basicity} = \frac{\text{CaO} + \text{MgO} + \text{BaO} + \text{K}_2\text{O} + \text{Li}_2\text{O} + \text{CaF}_2 + 0.5(\text{MnO} + \text{FeO})}{\text{SiO}_2 + 0.5(\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{ZrO}_2)} \quad (2)$$

In welding, the slag basicity has been shown to correlate the weld metal chemical composition to the chemical composition of the slag. In general, weld metal oxygen levels decrease with an increase in flux basicity (Ref. 9).

The basicity index of a flux also has a

J. DU PLESSIS is manager, Consultancy Services, Southern African Institute of Welding, Johannesburg, South Africa. M. DU TOIT is associate professor and P. C. PISTORIUS is professor, Department of Materials Science and Metallurgical Engineering, University of Pretoria, Pretoria, South Africa.

KEYWORDS

Shielded Metal Arc Welding
C-Mn Steels
Hydrogen-Assisted Cracking
Flux Additions

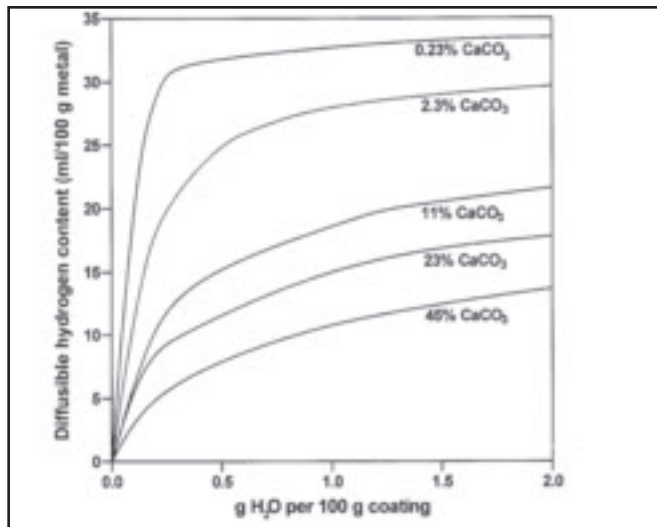


Fig. 1 — The effect of CaCO_3 in the electrode coating on the diffusible weld metal hydrogen content (Ref. 10).

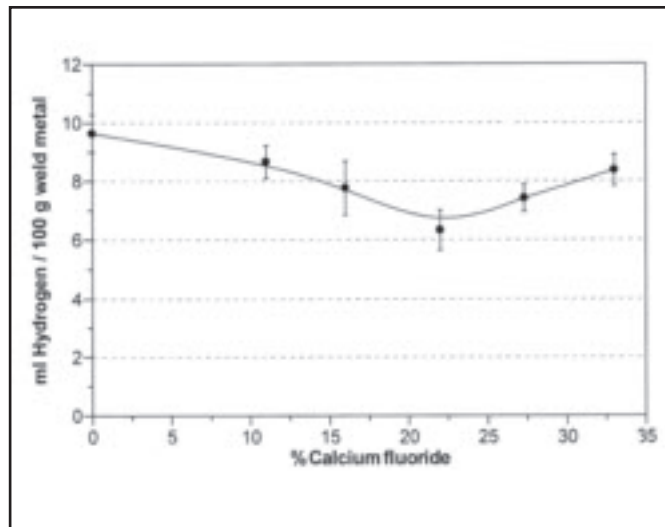


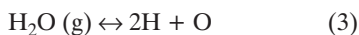
Fig. 2 — The influence of fluorspar (CaF_2) on the weld hydrogen content (each data point represents the average of five or six measurements, shown with the 95% confidence interval).

Table 1 — The Raw Material Ingredients Added to Twelve Experimental Flux Formulations (wt-%)

Sample number	Ferrosilicon	CaF_2	TiO_2	Feldspar	Carbonate	Fe-powder	Mn
C1054	2.63	21.64	5.26	5.36	15.89	31.19	3.51
C1055	2.56	21.08	5.13	5.22	18.04	30.39	3.42
C1056	2.49	20.50	4.99	5.08	20.31	29.55	3.32
C1057	2.72	22.36	5.44	5.54	13.09	32.23	3.63
C1058	2.80	23.05	5.61	5.71	10.38	33.23	3.74
C1059	2.43	19.95	4.85	4.94	22.46	28.75	3.23
C2006	2.63	21.64	5.26	5.36	15.89	31.19	3.51
C2007	3.36	0.0	6.72	6.84	20.27	39.80	4.48
C2008	2.99	11.06	5.97	6.08	18.03	35.40	3.98
C2009	2.83	15.72	5.66	5.77	17.09	33.54	3.77
C2010	2.45	27.17	4.89	4.89	14.76	28.99	3.26
C2011	2.24	33.22	4.49	4.57	13.54	26.58	2.99

significant influence on the weld metal hydrogen content. Terashima et al. (Ref. 10) reported a reduction in diffusible hydrogen levels from 12 to 2 mL/100 g of weld metal with an increase in flux basicity from 0 to 3. Chew (Ref. 11) demonstrated a considerable reduction in weld metal hydrogen with an increase in the coating CaCO_3 content, as shown in Fig. 1. This reduction in hydrogen level is partly attributed to an increase in slag basicity as CaCO_3 decomposes to form CaO (a basic oxide) during welding.

Dissociation of CaCO_3 also introduces higher levels of oxygen into the arc atmosphere that contribute toward the observed lower hydrogen levels. The influence of oxygen on hydrogen absorption during welding can be explained on the basis of the decomposition of moisture in the arc atmosphere, represented by Equation 3.



According to Le Chatelier's principle,

an increase in the oxygen content of the arc atmosphere encourages Equation 3 to proceed to the left. This removes monatomic hydrogen from the arc atmosphere, effectively reducing the partial pressure of hydrogen in contact with the liquid weld metal. At the low hydrogen levels normally present in the arc atmosphere during SMAW with basic electrodes, Sieverts' law predicts a corresponding decrease in the absorbed hydrogen content of the weld metal.

Flux basicity can also be represented by the optical basicity, Λ . Sommerville (Ref. 12) demonstrated that the average optical basicity can be calculated from Equation 4 for any slag composition, where X is the equivalent cation fraction of each oxide in the flux formulation.

$$\Lambda = X_{\text{AOX}} \Lambda_{\text{AOX}} + X_{\text{BOX}} \Lambda_{\text{BOX}} + \dots \quad (4)$$

Excellent correlation between the optical basicity and the slag water capacity has been reported, and the water capacity

can be expressed as a function of the optical basicity using Equation 5 (Ref. 13). A more detailed discussion of the slag water capacity is given in the section titled The Water Vapor Solubility of Molten Slag.

$$\log C_{\text{H}_2\text{O}} = 12.04 - 32.63\Lambda + 32.71\Lambda^2 - 6.62\Lambda^3 \quad (5)$$

This suggests that the diffusible weld metal hydrogen content can be reduced by increasing the basicity of the flux formulation. It must, however, be emphasized that the flux basicity of SMAW electrodes cannot be changed arbitrarily, as the flux ingredients also influence the weld metal composition, mechanical properties, arc stability, arc force, weld pool viscosity, weld bead shape, and welding characteristics. The SMAW consumable manufacturer has to find a balance between the operational characteristics of the electrode and the as-deposited weld metal chemical,

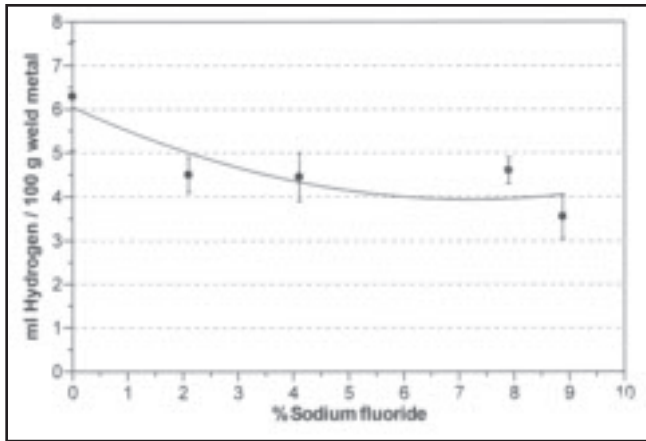


Fig. 3 — The influence of sodium fluoride (NaF) on the measured weld hydrogen content (with 95% confidence interval).

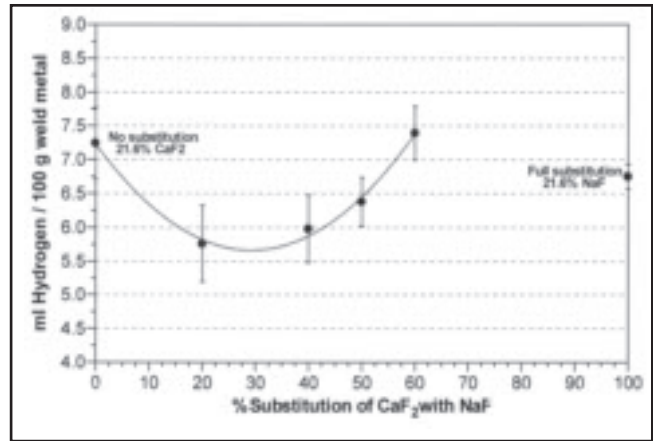


Fig. 4 — The influence of progressive substitution of fluorspar with sodium fluoride (each data point represents the average of between five and nine measurements, shown with the 95% confidence interval).

Table 2 — Chemical Analysis of the Slag Constituent of Each Weld (wt-%)

Sample number	SiO ₂	Al ₂ O ₃	Total Fe	Metallic Fe	TiO ₂	CaO	MgO	K ₂ O	MnO	F
C1054	18.1	2.20	2.31	0.69	9.49	38.8	5.77	2.20	2.21	13.5
C1055	19.3	2.24	2.29	0.58	9.50	41.4	5.92	2.28	2.37	13.5
C1056	17.4	2.19	2.64	1.22	9.35	43.1	5.79	1.79	2.38	12.9
C1057	18.6	2.37	1.90	0.86	10.2	39.7	6.21	2.40	2.38	14.7
C1058	18.1	2.29	2.07	1.02	10.5	38.0	6.31	2.52	2.69	15.4
C1059	19.2	2.09	3.15	1.28	8.74	42.6	5.41	1.88	2.62	12.1
C2006	17.3	2.20	1.67	1.30	10.3	41.3	6.00	2.30	2.02	15.3
C2007	24.3	3.44	6.94	2.94	16.4	23.4	9.19	2.59	5.12	0.20
C2008	17.9	2.31	3.52	2.56	9.34	41.7	5.65	1.90	2.35	14.6
C2009	20.2	2.69	2.75	2.25	11.2	36.8	6.44	2.17	2.39	11.1
C2010	14.1	1.78	2.34	1.62	8.94	44.1	5.27	1.89	1.85	18.1
C2011	12.6	1.58	2.49	2.31	7.44	46.7	4.55	1.96	1.62	19.5

physical, and mechanical properties. In order to optimize one property, another characteristic often has to be compromised.

The Addition of Fluoride-Containing Ingredients to the Flux Formulation

It is widely recognized that the addition of fluoride-containing compounds to the flux formulation reduces the diffusible weld metal hydrogen content. Fluoride present in the flux coating is reported to react with hydrogen to form reaction products that are insoluble in liquid iron (Ref. 2). As shown in Equation 6, an increase in fluoride content reduces the diffusible weld metal hydrogen content by promoting the formation of insoluble HF.



Fluorspar (CaF₂) is widely used as a flux constituent in basic-type electrodes. The fluoride in fluorspar reacts with hydrogen to form insoluble products, as demonstrated by Equation 6. In the presence of silica, fluorspar also reacts with

SiO₂ in the flux to form SiF₄, which functions as a shielding gas and reduces the partial pressure of hydrogen in the arc plasma (Ref. 14). This reaction is shown in Equation 7. The CaO formed as a product of reaction 7 is also expected to increase the basicity of the slag. All these mechanisms act in combination to reduce the diffusible weld metal hydrogen content.



The decomposition of CaF₂ during welding is, however, not particularly active and a significant fraction of the CaF₂ in the flux reports to the slag. The influence of alternative fluoride-containing compounds, such as sodium fluoride (NaF) or more complex compounds (including Na₃AlF₆, Na₂SiF₆, Na₂TiF₆, K₂SiF₆, K₂AlF₆, and K₂TiF₆), on the diffusible weld metal hydrogen level therefore needs to be examined.

The Water Vapor Solubility of Molten Slag

The amount of hydrogen absorbed by the molten weld metal from the arc at-

mosphere is strongly dependent on the water vapor solubility in the slag (or the slag hydroxyl capacity, C_{OH}) (Ref. 15). An increase in slag water capacity generally reduces the diffusible weld metal hydrogen content.

Ban-ya and coworkers (Ref. 15) reported that the activity coefficient of a component in a multicomponent slag can be described by a quadratic formalism based on the regular solution model. The activity coefficient of component *i* in a multicomponent regular solution can therefore be expressed as:

$$G_i = \Delta H_i = RT \ln \gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \quad (8)$$

where X_{*i*} is the cation fraction, and α_{*ij*} is the interaction energy between cations.

The hydroxyl capacity can be estimated from the regular solution (RS) model in the following way:

$$\frac{1}{2}H_2O = HO_{0.5} \text{ (RS)} \quad (9)$$

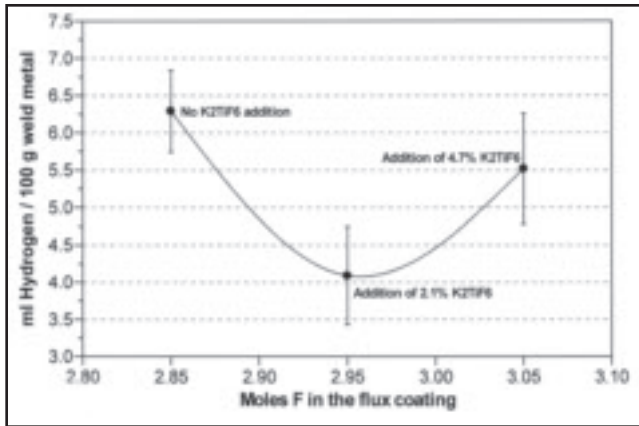


Fig. 5 — The influence of additions of K_2TiF_6 on the measured weld metal hydrogen content (each data point represents the average of seven measurements, shown with the 95% confidence interval).

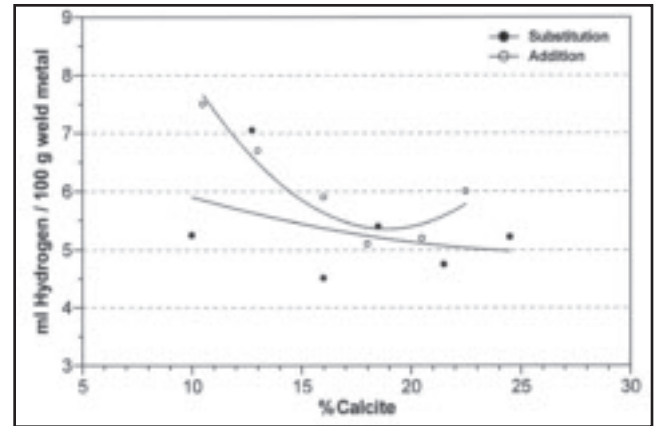


Fig. 6 — The influence of the calcite content of the flux formulation on the diffusible weld metal hydrogen content (each data point represents the average of 32 measurements).

$$RT \ln K_{H_2O} = RT \ln X_{HO_{0.5}} - 0.5 \log P_{H_2O} + RT \ln_{\gamma_{HO_{0.5}}} (RS) \quad (10)$$

The hydroxyl capacity can be expressed as

$$RT \ln C_{OH} = RT \ln K_{H_2O} - \sum_i \alpha_{H-i} X_i^2 - \sum_i \sum_j (\alpha_{H-i} + \alpha_{H-j} - \alpha_{ij}) \cdot X_i X_j \quad (11)$$

It is therefore possible to calculate the hydroxyl capacity of any slag composition as a function of temperature using Equation 11.

The water vapor solubility in slag is proportional to the square root of the water vapor pressure in the gas phase and the hydroxyl capacity is only a function of temperature and the slag composition. The hydroxyl capacity, C_{OH} , is therefore

given by Equation 12:

$$C_{OH} = \frac{\%H_2O}{\sqrt{\frac{P_{H_2O}}{P^0}}} \quad (12)$$

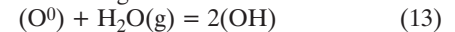
where $\%H_2O$ is the weight-percentage water in the slag, P_{H_2O} is the partial pressure of water vapor in the gas phase in equilibrium with the molten slag, and P^0 is atmospheric pressure.

Ban-ya et al. (Ref. 15) reported that the hydroxyl capacity decreases with an increase in slag basicity, but reaches a distinct minimum value at approximately unit basicity. At higher slag basicity levels, the hydroxyl capacity tends to increase.

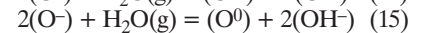
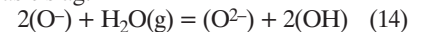
The dependence of the hydroxyl capacity on slag composition can be explained by a change in the state of water

vapor dissolved in the slag with changes in the slag basicity. Water vapor dissolves in molten slag in accordance with reactions 13 to 15, where (O^0) , (O^-) and (O^{2-}) represent bridging, nonbridging, and free oxygen ions, respectively, (OH) is the hydroxide, and (OH^-) the hydroxyl ion in the slag.

Acidic slag:



Basic slag:



Equation 13 represents the breakdown of silicate networks by hydroxyl ions in an acidic slag. Equations 14 and 15 represent the reaction of water vapor with free oxygen ions in a basic slag. In neutral basicity slag, neither of the mechanisms described in Equations 13 to 15 are favored, and the solubility of water vapor in the slag is minimized.

Table 3 — The Calculated Values of the Optical Basicity, Λ , and the Water Capacity, C_{H_2O} (ppm/atm^{0.5}), of Various Slag Chemistries

Sample number	Optical basicity, Λ	$\log C_{H_2O}$	C_{H_2O}	Weld metal hydrogen content
C1054	0.7472	3.1595	1443.742	5.8 mL/100 g
C1055	0.7486	3.1666	1467.737	4.8 mL/100 g
C1056	0.7600	3.2283	1691.585	5.7 mL/100 g
C1057	0.7467	3.1568	1434.903	6.2 mL/100 g
C1058	0.7456	3.1512	1416.292	7.5 mL/100 g
C1059	0.7525	3.1872	1538.956	5.5 mL/100 g
C2006	0.7559	3.2058	1606.128	6.3 mL/100 g
C2007	0.6804	2.8963	787.599	9.6 mL/100 g
C2008	0.7542	3.1964	1571.738	8.6 mL/100 g
C2009	0.7290	3.0716	1179.344	7.8 mL/100 g
C2010	0.7820	3.3606	2294.128	7.4 mL/100 g
C2011	0.8016	3.4919	3104.166	8.4 mL/100 g

Objectives of the Investigation

The hydrogen-reduction strategies described above suggest the possibility of reducing the diffusible hydrogen content of welds through a change in the coating composition of basic SMAW consumables. A series of experimental flux formulations was therefore designed on the basis of these hydrogen-reduction models, using the standard flux formulation of a basic-type E7018-1 SMAW electrode as reference. The influence of the following flux ingredients on the diffusible weld metal hydrogen content was evaluated:

- The addition of fluoride-containing ingredients (CaF_2 , NaF , and two complex fluoride-containing compounds: K_2TiF_6 and K_2AlF_6), and

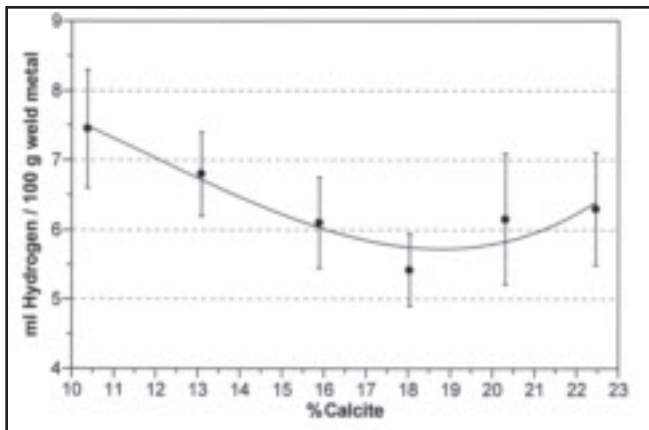


Fig. 7 — The influence of calcite additions to the flux formulation on the diffusible weld metal hydrogen content (with 95% confidence interval).

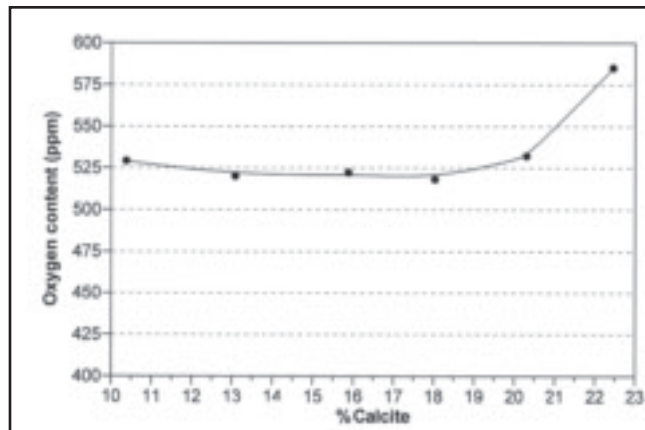


Fig. 8 — The influence of calcite additions to the flux formulation on the measured weld metal oxygen content.

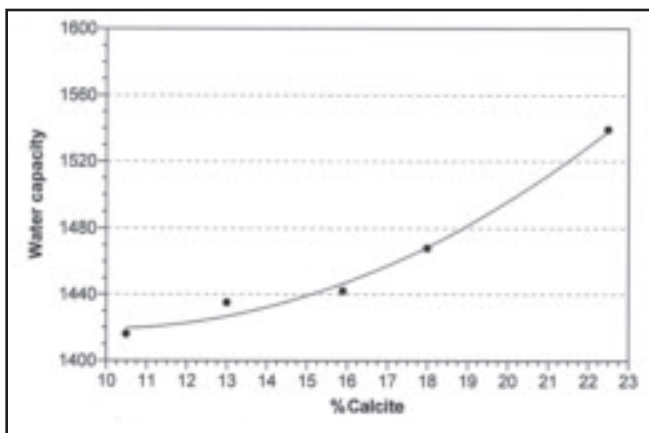


Fig. 9 — The relationship between the flux CaCO_3 content and the calculated water capacity of the slag ($\text{ppm/atm}^{0.5}$).

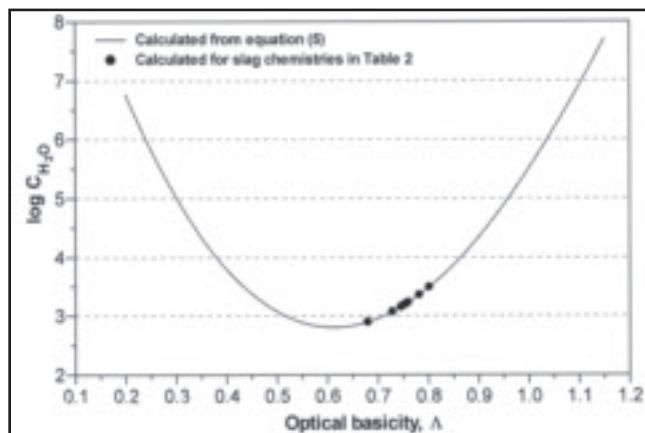


Fig. 10 — The slag water capacity, calculated from Equation 5, as a function of the optical basicity, including data points representing the experimental slag chemistries (from Tables 2 and 3).

- The addition of calcite, CaCO_3 .

The investigation focused on the influence of flux chemistry on the diffusible hydrogen content. The effect of variations in flux composition on the operating characteristics of the electrodes or the properties of the weld metal was not evaluated.

Experimental Procedure

Experimental Electrode Production

A series of experimental electrodes with different flux formulations was produced in small batches (1 kg flux each), utilizing raw materials typically used in the commercial production of SMAW electrodes.

As a reference, the coating composition of an E7018-1 basic-type welding electrode was selected. This flux formulation contains up to 16 different ingredients, with the following major coating constituents (as approximate percentages): Fluorspar (CaF_2) 22%

- Calcite (CaCO_3) and dolomite

- (CaCO_3 , MgCO_3) 20%
- Iron powder 31%
- Slag formers, binders, extrusion aids, and deoxidizers 27%

The raw materials were weighed and mixed in dry form for 7 min to obtain a homogeneous mixture. Raw materials from the same batches were used throughout the investigation. A liquid silicate binder was added to the dry flux mixture, followed by further mixing for 10 min. The flux was then extruded onto 4-mm-diameter mild steel core wire using a coating factor of 1.67. Core wire from the same cast was used for all the experimental electrodes. After extrusion, the electrodes were air dried for 24 h and then baked for 2 h at 180°C , followed by an additional 2 h at 460°C .

The weld metal hydrogen content for each electrode was determined using the procedure described in ISO 3690, *Procedure for Determining the Hydrogen Content in Arc Weld Metal*, but a Yanaco G-1006H gas chromatograph was used to measure the diffusible weld metal hydrogen con-

tent, instead of the traditional mercury method. After measuring the amount of weld metal hydrogen, the values were corrected for standard temperature, atmospheric pressure, and humidity conditions.

Experimental Electrode Formulation

The experimental flux formulations were designed to examine the influence of various fluoride-containing compounds and calcite flux additions on the diffusible weld metal hydrogen content. Descriptions of the experimental flux formulations follow, with all amounts expressed as weight percentages.

The Influence of Fluoride-Containing Compounds on the Weld Metal Hydrogen Content

The influence of fluoride-containing flux compounds on the weld metal hydrogen content was examined by the following:

- Varying the amount of fluorspar (CaF_2) in the flux coating from 0% to 34%,
- Adding sodium fluoride (NaF) to the

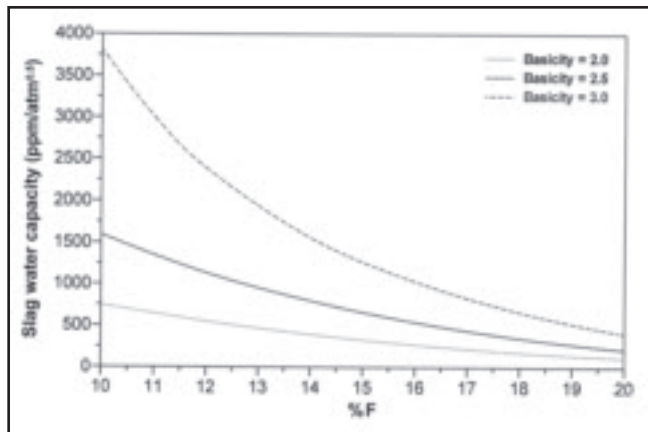


Fig. 11 — Calculated water capacity of welding slags with different fluoride contents and basicities. The basicity is $(\%CaO)/(\%SiO_2)$. In addition to the variable contents of SiO_2 , CaO , and CaF_2 , the slag was taken to contain constant mass percentages of Al_2O_3 (2%), FeO (4%), TiO_2 (11%), MgO (6%), and Na_2O (1.5%).

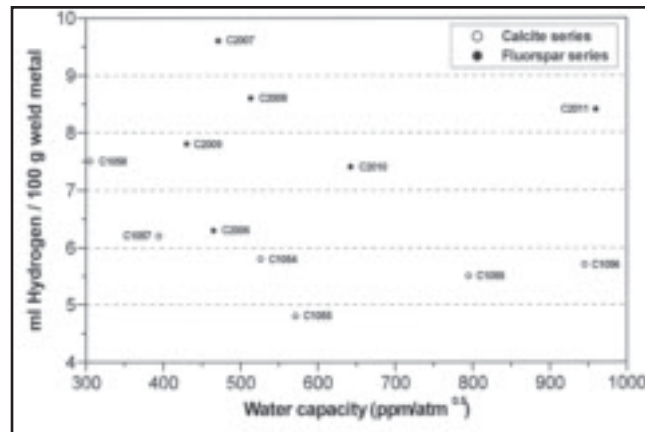


Fig. 12 — The relationship between the calculated slag water capacity (from the FACTSage slag model) and the measured weld metal hydrogen content of experimental electrodes with compositions shown in Table 1.

- reference flux coating in amounts ranging from 0% to approximately 8.9%.
- Progressively substituting the fluorspar in the flux coating with NaF, keeping the combined CaF_2 and NaF content constant at approximately 21.6%, and
- Adding K_2TiF_6 (2.1% and 4.7%, respectively) and K_2AlF_6 (4.7% and 8.9%, respectively) to the reference flux formulation.

The Influence of Calcite Additions on the Weld Metal Hydrogen Content

The influence of variations in the flux calcite ($CaCO_3$) content on the weld metal hydrogen level was investigated by varying the percentage calcite in the formulation from 10% to almost 24%. This was done by

- Adding between 10% and 24% $CaCO_3$ to the reference flux formulation, and
- Partially substituting the iron powder in the reference flux formulation by between 10% and 24% $CaCO_3$.

Results and Discussion

Diffusible Weld Metal Hydrogen Contents

The Influence of Fluorspar (CaF_2)

As shown in Fig. 2, the addition of up to 22% CaF_2 to the flux formulation reduced the diffusible weld metal hydrogen content. The addition of 22% CaF_2 to the formulation reduced the average weld metal hydrogen content by about 30%, compared to that of a formulation with no fluorspar. Additions of more than 22% CaF_2 increased the hydrogen content measured in the weld metal.

In the absence of high levels of SiO_2 in

the flux, the dominant hydrogen removal reaction due to CaF_2 is given by Equation 6. The HF compound is insoluble in the weld metal and is assumed to escape into the atmosphere during welding, reducing the weld hydrogen content. An increase in fluorspar is also expected to raise the flux basicity, further decreasing the weld hydrogen content. The results displayed in Fig. 2 are therefore in agreement with predicted theory up to a flux fluorspar content of approximately 22%.

The effect of increasing CaF_2 on the arc stability and the droplet transfer was not measured but it is expected to result in a decrease in arc stability at very high levels of CaF_2 . The decrease in arc stability would negatively influence the measured amount of weld metal hydrogen.

The Influence of Sodium Fluoride (NaF)

As shown in Fig. 3, the addition of NaF to the reference flux formulation reduced the diffusible weld hydrogen content. The presence of 8.9% NaF resulted in a 40% reduction in the measured weld hydrogen content. The mechanism of hydrogen reduction in the presence of NaF is similar to that described earlier for CaF_2 . Sodium fluoride dissociates in the arc to form fluoride and sodium ions. The fluoride reacts with hydrogen to form insoluble HF, thereby reducing the weld metal hydrogen content.

Substitution of Fluorspar with Sodium Fluoride (NaF)

The results of the substitution experiments are displayed in Fig. 4. A 20% substitution of fluorspar with NaF resulted in a reduction of approximately 25% in the weld metal hydrogen content. Fluorspar is

known to dissociate poorly in the arc, whereas NaF dissociates more readily and releases more fluoride. Higher levels of fluoride are therefore available in the arc to react with hydrogen.

Substitution of up to 50% resulted in average weld metal hydrogen levels below those obtained with no substitution. Substitution above 20%, however, progressively increased the measured weld hydrogen contents. This can be attributed to a reduction in the total molar amount of fluorine present in the flux. Although NaF dissociates more easily than fluorspar, it only contains half the molar amount of fluorine.

The effect of substitution between 60% and 99% did not form part of the investigation.

The Influence of K_2TiF_6 and K_2AlF_6 Additions

The results obtained for flux formulations containing K_2TiF_6 are displayed in Fig. 5. The addition of 2.1% K_2TiF_6 resulted in a decrease of approximately 30% in the measured weld metal hydrogen content. This decrease can be attributed to more fluoride being available to react with hydrogen. The base formulation contains 2.85 moles of fluorine as CaF_2 . Adding 2.1% K_2TiF_6 increased the molar amount of fluorine to 2.95. A further increase in K_2TiF_6 to 4.65% increased the amount of fluorine to 3.05 moles, but resulted in a significant increase in weld metal hydrogen.

K_2AlF_6 was added to the reference flux formulation in amounts of 4.7% and 8.9%, resulting in a slight increase in the weld metal hydrogen content. This is contrary to the theoretical prediction that more fluoride should be available in the presence of K_2AlF_6 to react with hydrogen to re-

duce the weld metal hydrogen content. The addition of K_2AlF_6 increases the total molar amount of fluorine, and results in a larger fraction of easily dissociated fluoride-containing compounds in the flux.

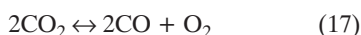
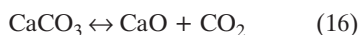
Matsushita and Liu (Ref. 2) described a similar trend on addition of K_2AlF_6 to flux cored wires, reporting a decrease in weld metal hydrogen content with the addition of up to 5% K_2AlF_6 . With higher levels of K_2AlF_6 in the flux, no further decrease was observed and a slight increase in hydrogen content was reported. This effect is due to the decrease in slag basicity observed with the decomposition of the complex fluorides. The complex potassium fluorides form Al and Ti oxides during decomposition, which results in lower slag basicity. It is postulated that a similar trend would have been observed in the current investigation if a wider range of K_2AlF_6 contents had been examined.

The Influence of Calcite ($CaCO_3$)

As shown in Fig. 6, similar trends were observed on merely adding calcite to the reference formulation and on partially substituting iron powder with calcite. An increase in calcite content initially reduced the weld metal hydrogen content, but this trend appeared to reverse at higher levels of calcite. Balancing the formulation with iron powder, compared to merely adding calcite, resulted in the hydrogen curve being shifted to lower hydrogen levels. This can be ascribed to an increase in the weld metal oxygen content, which lowers the weld metal hydrogen content (as illustrated by Equation 3).

The relationship between calcite additions and the weld metal hydrogen content appeared to be largely linear up to about 18% calcite in the flux formulation. With further additions of calcite, the weld metal hydrogen content increased, as shown in Fig. 7. This suggests that the decomposition of calcite in the welding arc no longer acted as the dominant reaction controlling the absorption of hydrogen from the arc plasma.

The influence of calcite additions to the flux formulation on the weld metal oxygen content is illustrated in Fig. 8. As shown in Equations 16 and 17, calcite decomposes in the arc to form CaO, CO, and CO_2 .



CaO increases the basicity of the slag system, which should decrease the amount of weld metal hydrogen. The presence of CO and CO_2 in the arc atmosphere reduces the partial pressure of hydrogen, which should also reduce the diffusible weld

metal hydrogen content. As shown in Fig. 8, the measured weld metal oxygen content remained relatively stable with additions of up to 18% calcite to the flux formulation. Further additions of calcite resulted in an increase in the weld metal oxygen content. This increase in weld metal oxygen content coincides with the observed increase in weld metal hydrogen content.

These results suggest that there are a number of competing mechanisms controlling the weld metal hydrogen content. Although it is difficult to isolate the individual contributions of the different mechanisms, an attempt will be made to understand the individual reactions that occur in the weld metal and slag by examining the influence of flux composition on the optical basicity and water capacity of the slag.

Evaluation of the Hydroxyl Capacity and Optical Basicity of the Slag

In order to explain the tendency of the weld metal hydrogen content to pass through a minimum on addition of fluoride-containing compounds and calcite to the electrode flux formulation, the hydroxyl capacity and the optical basicity of a number of experimental flux formulations were calculated. The approximate compositions of these flux formulations are given in Table 1. The weld metal composition and slag chemistry of each of the welds deposited using these electrodes were analyzed. The measured slag compositions are shown in Table 2.

The optical basicity and the hydroxyl capacity of each slag were then calculated from Equations 4, 5, 11, and 12. The results of these calculations are presented in Table 3, and illustrate the relationship between optical basicity, water capacity, slag chemistry, and the as-deposited weld metal hydrogen content.

As shown in Fig. 9, higher levels of $CaCO_3$ in the flux cause the amount of CaO in the slag to increase and also raise the optical slag basicity, resulting in an increase in the slag water capacity. The effect of additions of CaF_2 to the flux formulation is less evident, due to variations in both the $CaCO_3$ content and the CaF_2 content of the experimental formulations.

A minimum in water vapor solubility has been reported near neutral basicity in many slag systems (Ref. 15). When the empirical relationship between the slag water capacity and optical basicity represented by Equation 5 is shown graphically, however, the minimum is observed to occur at approximately 0.6 — Fig. 10. Also shown in Fig. 10 are data points representing the calculated water capacity and optical basicity of each slag chemistry (from Table 3). These data points are all located in the vicinity of the minimum in slag water capacity, but the results shown in this

figure do not account for the minima observed in the diffusible weld metal hydrogen contents on addition of fluoride-containing compounds and $CaCO_3$ to the flux.

The correlation between optical basicity and slag water capacity represented by Equation 5 and shown graphically in Fig. 10 originated from results for binary and ternary slags containing CaO, SiO_2 , MgO, and Al_2O_3 under steelmaking conditions (Ref. 13). The slag chemistries shown in Table 2 are considerably more complex, which may influence the relationship between the basicity and slag water capacity. For better prediction in the present case, the slag model "FACT-SLAG?" of FACT-Sage was used. The model considered the slag as a solution of the species SiO_2 , TiO_2 , CaO, FeO, Na_2O , Al_2O_3 , MgO, NaF, CaF_2 , MgF_2 , FeF_2 , H_2O , NaOH, $Ca(OH)_2$, $Mg(OH)_2$, and $Fe(OH)_2$. The molten slag was conceptually equilibrated with a large excess of gas containing 1% (by volume) H_2O in Ar. The calculated total water content of the slag (as hydroxide or dissolved water) was then used to calculate the water capacity, C_{H_2O} , from Equation 18. Since not all the species present in the welding slag are included in the slag model, some substitutions had to be made. For this calculation, MnO was included in the calculation as an equivalent amount (mole for mole) of FeO, SrO was included as CaO, and K_2O as Na_2O .

$$C_{H_2O} = \frac{\text{ppm } H_2O}{\sqrt{P_{H_2O}}} \quad (18)$$

In order to highlight the predictions of the model, Figure 11 displays the calculated water capacity as a function of slag basicity and fluoride content. In this figure, the basicity is given by $(\%CaO)/(\%SiO_2)$, where "CaO" refers to the total calcium content of the slag (whether present as CaO or as CaF_2). Figure 11 illustrates that the slag water capacity is a strong function of the slag basicity, with an increase in basicity resulting in higher slag water capacities for the range of chemistries evaluated. The slag water capacity is, however, also determined by the slag fluoride content. At a constant basicity, substitution of CaO with CaF_2 (resulting in an increase in slag fluoride content) decreases the water capacity.

Although theory predicts that increasing slag basicity and higher flux CaF_2 levels should decrease the weld metal hydrogen content, Fig. 11 illustrates that an increase in the slag fluoride content reduces the slag water capacity. This can be attributed to the relative contributions of CaF_2 and CaO toward increasing the slag

basicity. Even though Equation 2 predicts that CaF_2 increases the slag basicity to the same extent as CaO , its effect on the optical slag basicity is less pronounced (estimated Λ_{th} values for CaF_2 range from 0.43 to 0.67, compared to 1.0 for CaO (Ref. 13)). The addition of CaF_2 to the flux formulation, resulting in higher levels of fluoride in the slag, therefore, dilutes the beneficial effect of CaO on the slag optical basicity and water capacity. A decrease in the slag water capacity tends to increase the diffusible weld metal hydrogen content, as shown in Fig. 12. The predicted decrease in slag water capacity with higher levels of fluoride in the slag may account for the higher weld metal hydrogen contents observed on addition of high concentrations of fluoride-containing compounds to the flux.

The data points labeled "calcite series" in Fig. 12 demonstrate the influence of increasing flux calcite content (at fairly constant levels of CaF_2) on the slag water capacity and weld metal hydrogen content. Increasing additions of CaCO_3 to these flux formulations tend to raise the slag basicity, causing an increase in the slag water capacity and a reduction in the measured weld metal hydrogen level.

The data points in the "fluorspar" series in Fig. 12 display considerably more scatter. This can be attributed to variations in both the CaCO_3 content (from 13.54% to 20.27%) and the CaF_2 content (from 0% to 33.22%) of the flux formulations, resulting in a wide range of slag basicities and fluoride contents. Although the slags in this series tend to be more basic than the slags in the calcite series (with the exception of fluxes with very low CaF_2 levels, i.e., samples C2007 and C2008), the slag water capacities are generally lower and the weld hydrogen contents higher. (Even though sample C2011 has a high slag fluoride content, its basicity is disproportionately high, which may account for its high water capacity). This confirms the earlier prediction that high slag fluoride levels may reduce the slag water capacity, even though CaF_2 additions to the slag is reported to raise the slag basicity.

Conclusions

The results of this investigation confirm that arc chemistry modifications brought about by changes in the electrode flux composition can influence the diffusible weld metal hydrogen content of steel welds to a significant extent.

The addition of fluoride-containing compounds (CaF_2 , NaF , K_2TiF_6 , or K_2AlF_6) to the reference E7018-1 basic-type flux formulation initially resulted in a reduction in the diffusible weld metal hydro-

drogen content. The addition of 22% fluorspar to the flux lowered the average weld metal hydrogen content by about 30%, while the addition of 8.9% NaF resulted in a reduction of approximately 40%. The measured weld metal hydrogen content on addition of K_2TiF_6 or K_2AlF_6 followed a similar trend. High concentrations of these complex fluoride-containing compounds in the flux seemed to cause an increase in the diffusible weld metal hydrogen content.

Additions of up to 18% calcite (CaCO_3) to the reference flux formulation gave rise to a reduction in the weld hydrogen content, but this trend appeared to reverse at higher levels of calcite. The beneficial influence of up to 18% calcite in the flux formulation can be attributed to the formation of CaO , CO , and CO_2 as products of the dissociation of CaCO_3 in the arc. CaO increases the basicity of the slag, while the presence of CO and CO_2 in the arc atmosphere reduces the partial pressure of hydrogen.

The results of this investigation revealed that the diffusible weld metal hydrogen content decreased to a minimum on addition of increasing amounts of CaCO_3 and fluoride-containing ingredients to the flux formulation. Higher levels of these ingredients caused an increase in the weld hydrogen content. This behavior can be ascribed to a number of complex reactions, dominated by the amphoteric behavior of water vapor in the slag and the relationship between the hydroxyl ion capacity and the oxide activity of the slag.

The slag water capacity was calculated for a number of slag chemistries measured for experimental flux formulations containing varying amounts of CaCO_3 and CaF_2 . These calculations showed that the slag water capacity is a strong function, not only of the slag basicity, but also of the slag fluoride content. At constant basicity, an increase in slag fluoride content, brought about by higher levels of CaF_2 in the flux formulation, decreases the slag water capacity and may result in higher weld metal hydrogen contents. The predicted decrease in slag water capacity with higher levels of fluoride in the slag may therefore account for the higher weld metal hydrogen contents observed on addition of high concentrations of fluoride-containing compounds to the flux.

Acknowledgments

Special thanks to the Afrox Welding Consumable Factory for producing the experimental electrodes and performing the weld metal chemical analyses.

References

1. Davidson, J. L. 1998. Advances in hydro-

gen management: The science-based design of low hydrogen consumables for the future. *Australian Welding Journal* 43: 33-39.

2. Matsushita, M., and Liu, S. 2000. Hydrogen control in steel weld metal by means of fluoride additions in welding flux. *Welding Journal* 79(10): 295-s to 303-s.

3. Fleming, D. A., Bracarense, A. Q., Liu, S., and Olson, D.L. 1996. Toward developing a SMA welding electrode for HSLA-100 grade steel. *Welding Journal* 75(6): 171-s to 183-s.

4. Liu, S., Olson, D. L., and Ibarra, S. 1994. Electrode formulation to reduce weld metal hydrogen and porosity. *Proceedings of the 13th International Conference on Offshore Mechanics and Arctic Engineering* 3: 291-298.

5. Rowe, M. D., Liu, S., and Reynolds, T. J. 2002. The effect of ferro-alloy additions and depth on the quality of underwater wet welds. *Welding Journal* 81(8): 156-s to 166-s.

6. Pokhodnya, I. K., Patsevich, A. P., Golovko, V. V., and Koteltchouk, A.S. 1999. Technology and metallurgy methods for decreasing diffusible hydrogen content. *Welding in the World*, Vol. 3, No. 4, pp. 81-90.

7. Baune, E., Bonnet, C., and Liu, S. 2000. Reconsidering the basicity of a FCAW consumable — Part 2: Verification of the flux/slag analysis methodology for weld metal oxygen control. *Welding Journal* 79(3): 66-s to 71-s.

8. Tuliani, S. S., Boiszewski, T., and Eaton, N. F. 1969. Notch toughness of commercial submerged arc weld metal. *Welding and Metal Fabrication* 8: 327-339.

9. Datta, I., and Parekh, M. 1989. Filler metal flux basicity determination using the optical basicity index. *Welding Journal* 68(2): 68-s to 74-s.

10. Terashima, H., and Tsuboi, J. 1976. Hydrogen in submerged arc weld metal produced with agglomerated flux. *Welding Journal of Japan* 45: 28-33.

11. Chew, B. 1973. Prediction of weld metal hydrogen levels obtained under test conditions. *Welding Journal* 52(9): 386-s to 391-s.

12. Sommerville, I. D., and Yang, Y. 2001. Basicity of metallurgical slags. *AusIMM Proceedings* 306(1): 71-77.

13. *Slag Atlas*, 2nd edition. 1995. Edited by the Verein Deutsche Eisenhüttenleute (VDEh). 11-14, Düsseldorf, Verlag Stahleisen GmbH.

14. Kuzmenko, V. G., and Guzej, V. I. 2005. Pore formation in weld metal in submerged arc welding with surface saturation of grains with fluorine. *The Paton Welding Journal* 2: 14-17.

15. Ban-Ya, S., Hino, M., and Nagasaka, T. 1993. Estimation of water vapour solubility in molten silicates by quadratic formalism based on the regular solution model. *ISIJ International* 33(1): 12 to 19.