



# HYGROSCOPICITY OF HIGH-BASICITY SYNTHETIC FLUX

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It was experimentally found that hygroscopicity of synthetic acid fluxes is at the same that of standard fused fluxes. Hygroscopicity of the synthetic fluxes grows not less than 10 times with increase in their basicity from 0.8 to 2.4. This probably is caused by the presence of a free lime which forms in the synthetic flux as a result of the solid-phase reaction between magnesium oxide and calcium fluoride in flux sintering. The thermodynamic calculation results and experimental data confirm the above assumption.

**Keywords:** *welding flux, oxide-fluoride system, basicity, hygroscopicity, phase composition, solid-phase chemical reaction*

Development of welding fluxes obtained by means of a solid-phase synthesis of initial charge components and mechanical refinement of fused product per granules [1] is an important result of investigations, carried out in the E.O. Paton Electric Welding Institute.

Deterioration of welding-technological properties of the fluxes can be caused by increase of their basicity. Indicated tendency was also noted for a synthetic flux. Thus, some degradation of forming capability of the flux, tarnish of a weld surface, and in some cases, appearance of single pores were found after relatively short soaking of SFT-6 flux (TU PWI 839–93) with  $B_{IIW} = 2.4$  basicity under humid atmospheric conditions during surfacing of low alloy heat-resistant steel. These drawbacks were eliminated after repeated baking of such a flux at 550–600 °C for 2 h. Soaking in humid atmosphere of the low-basicity synthetic fluxes, for example, pilot flux SF-1 ( $B_{IIW} = 0.8$ ) does not result in notable degradation of welding-technological properties. It can be assumed, therefore, that the synthetic fluxes, like others, obtain higher hygroscopicity with increase of basicity.

The aim of the present work lies in experimental determination of hygroscopicity of SFT-6 type syn-

thetic fluxes of MgO–CaF<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system and reasons of its increase at basicity rise. Hygroscopicity of the standard fluxes of other types (agglomerated, fused vitreous fluxes and fused honeycombed ones), as well as low basicity of the synthetic flux, was determined for comparative assessment.

The charge components from Table 1 were selected for manufacture of the synthetic fluxes (objects of investigation of this study). A gravimetric method was used for determination of hygroscopicity of the fluxes.

Several forms of moisture differing by type and energy of bonding between the atoms of hydrogen, oxygen and flux material [2] can be, symbolically, distinguished in the fluxes. Temperature of thermal desorption of the moisture from the flux is determined by value of indicated energy. Most of chemically bound moisture (around 80 %) in the fused fluxes granulated by pouring of a melt in a water refers to high-temperature form and is removed at temperature values of 800–1000 °C [2]. There is no high-temperature form of the moisture in the fluxes having no exposure of «wet» granulation.

Content of moisture in the fluxes is determined by standard method [3] allowing setting general (gross) moisture emission from the flux in the temperature interval from 20 to 1000 °C. However, the hygroscopicity of fluxes is to be evaluated considering the

**Table 1.** Some charge materials used for production of the synthetic fluxes

Charge materials	Main component of the material	Grade	Normative document (GOST)
Periclase fused powder for steel-making production (magnesite)	MgO	PPK-88	24862–81
Fluor-spar lump concentrate (fluorite)	CaF <sub>2</sub>	FKS-95A	4421–73
Alumina	Al <sub>2</sub> O <sub>3</sub>	GK	6912–87
Feldspar for electrode coatings	NaK[AlSi <sub>3</sub> O <sub>8</sub> ]	PShM	4422–73
Glass breakage*	Na <sub>2</sub> O–CaO–6SiO <sub>2</sub>	–	–
Quartz sand	SiO <sub>2</sub>	PB-150-1	22551–77
Manganese ore concentrate for electrode coating	MnO	–	4418–75
Metallic manganese	Mn	Mn95	6008–90
Calcium quicklime	CaO	Grade 1	9179–77
Crystalline foundry graphite	C	GL-1	5279–74

\* Powder material, product of soda-lime glass milling being a spoilage and wastes of production of houseware and ornamental glass products according to GOST 24315–80 and(or) flat glass according to GOST 111–2001.

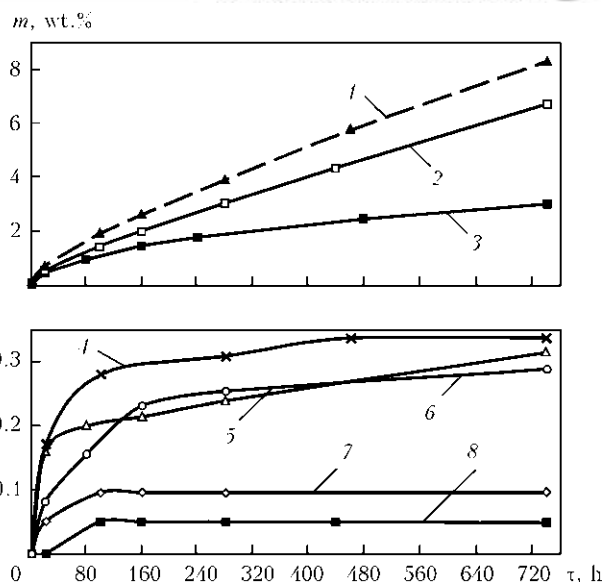


stated task, i.e. their capability to water absorption after repeated baking and at further soaking in the atmosphere. The fluxes, significantly differing by method of manufacture and, therefore, containing constantly unknown amount of the moisture of different forms, were the objects of investigation. In consideration of mentioned above application of the method, described in [3], will inevitably lead to obtaining of the numerical results which are difficult for interpretation and reasonable comparison without performance of large number of additional experiments. The moisture, absorbed by the fluxes in the course of this experiment, in each case would be an undetermined item in a level of its gross emission, determined by the method given in [3]. At the same time, soaking of small portions (samples) of the fluxes in the atmosphere with given relative humidity and determining increase of their mass by means of weighting before and after soaking as, for example, in study [4], allow more easily evaluating the flux hygroscopicity.

Baking of agglomerated flux OK 10.63 at 300 °C during 2 h was carried out before the experiment (recommendation of the manufacturer – ESAB, Sweden). Fused AN-43, AN-67B, AN-66 and synthetic SF-1 fluxes were baked at 400 °C for 2 h and fluxes AN-22M and SFT-6 were treated at 570 °C for 2 h (taking into account the general recommendations of operation [5]). Initial weighting of the samples of indicated fluxes of 30–80 g weight was performed immediately after baking and cooling to temperature close to room one. Then, the samples were put in the atmosphere, created in a tightly closed exiccator with water on a bottom, and soak at 20–25 °C. Thickness of layer of the fluxes in the samples was equal 12–15 mm. Size of the flux grains made 0.63–2 mm. The samples were weighted using an analytical balance and set of weights of the 4th class of accuracy according to GOST 7328–61. Results of the experiments are shown in the Figure and Table 2. They give the values of the basicity calculated on IIW formulae [6] using the average weight fractions of components on data of corresponding normative documents. It follows from the Figure that the hygroscopicity of synthetic flux SFT-6 (curve 2) only 19 % lower than that of agglomerated flux OK 10.63 (curve 1) during 744 h of soaking.

Further, the following changes were introduced in a standard production technology of the high-basicity synthetic flux: heating and cooling of sintered charge with furnace, increase of maximum sintering temperature from 1050 to 1160 °C and duration of soaking at maximum temperature from 1 to 2 h. Hygroscopicity of the high-basicity synthetic flux of basic composition, sintered on changed technology (Table 2, flux B1; Figure 1, curve 3), was 2.2 times lower than in flux SFT-6. However, hygroscopicity of the synthetic flux at that remains significantly higher than that of the most hygroscopic from the fused fluxes, i.e. honeycombed flux of AN-66 grade. Hygroscopicity of the low-basicity synthetic flux SF-1 is comparable with that of the fused ones.

It should be noted that the general (gross) level of absorption of different forms of the moisture by



Kinetics of absorption of the moisture by welding fluxes: 1 – OK 10.63; 2 – SFT-6; 3 – B1; 4 – AN-66; 5 – AN-22M; 6 – SF-1; 7 – AN-67B; 8 – AN-43 (*m* – relative increase of weight)

flux is characterized by specific values of weight increase of the samples. Portion of the moisture, absorbed by surface of grains and pores, and being removed at temperature from 20 to 200 °C makes only 5 % in the fused fluxes of AN 348A type. 15 % of total amount of the moisture, which should, apparently, be referred to sorbed and zeolite forms, is removed in 20–600 °C interval. The main amount of the moisture is removed from flux at heating above 800 °C and refers to chemically bound form of hydroxyl group type [2]. Only application of special methods of the investigation can provide accurate ratio in distribution of different forms of the moisture, absorbed by the synthetic fluxes. At the same time, portion of the moisture, absorbed by surface of the grains and micropores of the synthetic fluxes, is supposed to have the same order that in the fused ones. Elimination of appearance of zeolites in the synthetic flux due to significant difference of the conditions of their natural and industrial synthesis [7] from the conditions of synthetic flux sintering [1] is also to be considered. Therefore, it is assumed for the future that portion of the sorbed moisture is neglected due to its small

Table 2. Hygroscopicity of the fluxes of different types

Flux grade	Flux type	Flux basicity $B_{IIW}$	Hygroscopicity*, wt.%
OK 10.63	Agglomerated	2.56	8.4
SFT-6	Synthetic	2.40	6.8
B1	Same	2.40	3.08
AN-66	Honeycombed fused	0.97	0.34
AN-22M	Vitreous fused	1.35	0.32
SF-1	Synthetic	0.80	0.29
AN-67B	Vitreous fused	1.04	0.097
AN-43	Same	1.12	0.050

\*Hygroscopicity during of soaking in humid atmosphere for 774 h.



amount and all moisture, absorbed by the synthetic flux, is referred to chemically-bound form.

Thus, rapid (10–23 times) increase of hygroscopicity of the synthetic flux was promoted by a change of component composition and basicity, represented in Table 3. It was supposed based on these data and taking into account specified remarks that appearance of the compounds having tendency to hydration in a finished flux and causing a rise of the flux susceptibility to moisture absorption (similar to silicate-lump in the agglomerated fluxes) was contributed by such a change of component composition. In this connection an investigation of phase composition of SFT-6 flux was of interest.

X-ray phase analysis of SFT-6 flux carried using DRON-UM1 diffractometer in monochromatic  $CuK_{\alpha}$  irradiation by step-by-step scanning method (accelerating voltage 35 kV, current 25 mA) allowed determining the main components of its phase composition, i.e. fluorite  $CaF_2$ , alumomagnesite spinel  $MgO \cdot Al_2O_3$ , forsterite  $2MgO \cdot SiO_2$ , cuspidine  $3CaO \cdot 2SiO_2 \cdot CaF_2$  and free MgO. Small and trace amounts of diopside  $CaO \cdot MgO \cdot 2SiO_2$ , pseudo-wollastonite  $\alpha-CaO \cdot SiO_2$  and other compounds are present in the flux. Nomenclature of the main components in SF-1 flux composition (for which the same analysis was performed [1]) does not correspond with the given one and includes nepheline  $\beta-Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ , enstatite  $MgO \cdot SiO_2$ , andalusite  $Al_2O_3 \cdot SiO_2$ , braunite  $MnO \cdot SiO_2$ , wollastonite  $\beta-CaO \cdot SiO_2$  and diopside.

Study of the compounds of SFT-6 flux being responsible for its high hygroscopicity will be carried out in the experimental way. For this a sintering of the simplified model charges consisting of fluorides and oxides is to be performed. The latter are taken in a compatible mole proportion corresponding to known minerals. Ratio of weight fraction of the fluoride to sum weight fraction of the oxides made 2:3 in the charge that is typical for the fluxes with high content of  $CaF_2$ . An output of the investigated compound is supposed to be maximum at such ratios and presence

of the necessary thermodynamic conditions. At the same time a reproduction of all peculiarities of solid-phase reactions between the components, which are stipulated by the presence of large amount of  $CaF_2$ , will be possible. Table 4 shows component composition of the charge. Charge materials given in Table 1 were used.

Granulated material with the same grain size as in earlier tested fluxes was obtained from the sintered charges by means of mechanical refinement and sieving. Further, hygroscopicity of the obtained granulated products was evaluated using indicated gravimetric method. Limit of the maximum soaking in humid atmosphere for all the samples made 336 h. Hygroscopicity of the separate charge components after their heat treatment using mode of sintering of model charges (maximum temperature 1125 °C; time of heating up to maximum temperature – 2 h; duration of soaking at maximum temperature – 2 h, heating and cooling with the furnace) was also determined taking into account the possibility of existence of real compounds of the unreacted components in a free state (for example, MgO,  $CaF_2$ ) in the fluxes.

Table 4 shows a relative increase of weight of the samples characterizing hygroscopicity of the sintered products. It was stated that hygroscopicity of phases of SFT-6 flux lies in the ranges from 0.07 for fluorite up to 0.50 wt.% for sintered mixture of fluorite + forsterite. It was noted that the hygroscopicity of a pure MgO (superpure according TU 6-09-2807-78) is an order higher than of fired magnesite. However, if theoretically decide that all magnesite in SFT-6 flux charge was chemically inert during sintering as well as obtained properties of pure MgO then its contribution in the increase of flux weight would make  $0.31 \cdot 2.6 = 0.81$  %. This is significantly lower of particularly registered hygroscopicity of SFT-6 flux under any conditions of sintering (2.0–3.5 wt.% during 336 h). It followed from these data that the sum contribution of mineral components of the SFT-6 synthetic flux cannot be an explanation of its increased

**Table 3.** Influence of component composition, basicity and parameters of sintering of the synthetic fluxes on their hygroscopicity\*

Flux grade	Weight fraction of components, %								Peculiarities of sintering	$B_{IIW}$	Hygroscopicity, wt. %
	Magnesite	Fluorite	Alumina	Feldspar	Glass breakage	Manganese ore	Metallic manganese	Graphite			
SF-1	5	15	20	–	50	10	–	–	Setting of a charge in the furnace, heated up to 950 °C, soaking at that temperature for 1 h, air cooling	0.8	0.29
SFT-6	31	26.25	16	23	–	–	1.75	2	Setting of a charge in the furnace, heated up to 1050 °C, soaking at that temperature for 1 h, air cooling	2.4	6.80
B1	31	26.25	16	23	–	–	1.75	2	Soaking of a charge at maximum temperature 1160 °C during 2 h, heating and cooling with furnace	2.4	3.08

\*Compared are the values of the hygroscopicity during soaking in humid atmosphere for 744 h.



**Table 4.** Composition and hygroscopicity of the sintered model charges

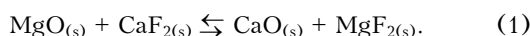
Charge grade	Fraction of components, wt.%								<i>m*</i> , wt.%
	Fluorite	Manganese oxide	Magnesite	Alumina	Lime	Feldspar	Quartz sand	Other components	
Flux basic composition									
SFT-6	26.25	–	31.0	16.0	–	23.0	–	Graphite 2.0; Mn 1.75	3.50
B1	26.25	–	31.0	16.0	–	23.0	–	Same	2.05
Charge with fluorite + alumomagnesite spinel MgO·Al <sub>2</sub> O <sub>3</sub>									
FSh	41.0	–	18.0	41.0	–	–	–	–	0.22
FSh-1**	36.9	–	16.2	36.9	–	10.0	–	–	0.21
Fluorite + forsterite 2MgO·SiO <sub>2</sub>									
FF	39.77	–	35.28	–	–	–	24.95	–	0.50
Fluorite + diopside CaO·MgO·2SiO <sub>2</sub>									
FD	39.0	–	12.0	–	17.0	–	32.0	–	0.47
Fluorite + wollastonite CaO·SiO <sub>2</sub>									
FV	40.0	–	–	–	29.0	–	31.0	–	0.13
Cuspidine 3CaO·2SiO <sub>2</sub> ·CaF <sub>2</sub>									
K	21.3	–	–	–	45.9	–	32.8	–	0.17
Fluosilicates with excessive and insufficient content of feldspar									
FS1	31.0	–	–	–	–	69.0	–	–	0.11
FS2	43.0	7.4	–	–	–	49.6	–	–	0.04
Fluorite + magnesite CaF <sub>2</sub> ·MgO									
FM	65.0	–	35.0	–	–	–	–	–	1.46
Charge components (lime, chemically pure MgO, alumina, magnesite, fluorite, feldspar)									
I	–	–	–	–	100	–	–	–	30.10
MgO	–	100	–	–	–	–	–	–	2.60
G	–	–	–	100	–	–	–	–	0.83
M	–	–	100	–	–	–	–	–	0.21
F	100	–	–	–	–	–	–	–	0.07
PSh	–	–	–	–	–	100	–	–	0.04

\*Relative increase in weight of the granulated product samples for the period of soaking in humid atmosphere for 336 h. \*\*Charge with feldspar addition for improvement of sintering.

hygroscopicity. However, experimental data of [8] allowed assuming that a contribution of free lime CaO in composition of the finished flux creates the increased hygroscopicity of SFT-6 flux.

As shown in [8], free lime can be an intermediate product of chemical reaction between the CaF<sub>2</sub>, oxides and silicate-lump with formation and decay of complex oxyfluoride due to effect of anion redistribution mechanism between the calcium and magnesium during heating of a multicomponent charge of the agglomerated flux with excessive content of the acid oxides. Further, the lime appeared in such a flux is consumed for formation of anorthite mineral.

If possible intermediate reactions for formation of the magnesium and calcium oxyfluorides are omitted then a process of lime formation can be represented by more simple reaction



An equilibrium constant of such a reaction can be interpreted as

$$k_{\text{eq}} = (a_{\text{CaO}} \cdot a_{\text{MgF}_2}) / (a_{\text{CaF}_2} \cdot a_{\text{MgO}}), \quad (2)$$

where *a* is an activity of agents, indicated in the indices.

Temperature dependence of the equilibrium constant of this reaction can be calculated using an exact method of L.P. Vladimirov and reference value of variables [9]. Taking into account formulae (2) the obtained calculated values lg *k<sub>eq</sub>* from –3.027 up to –2.414 at temperatures from 800 to 1127 °C, respectively, indicate the appearance of several percents of products of reaction (1) in MgO<sub>(s)</sub>–CaF<sub>2(s)</sub> system after its continuous soaking at 1125 °C. Specified reaction has a tendency to intensify with temperature rise.

A model charge consisting of MgO and CaF<sub>2</sub> in 1:1 mole ratio was sintered for checking the possibility of formation of the free lime in reaction (1). Hygroscopicity of the sintered product made 1.46 wt.% during 336 h of soaking that, respectively, 7 and 21 times higher than in magnesite and fluorite, sintered individually (see Table 3). Obtained result indicates that a phase appears in the process of sintering in MgO<sub>(s)</sub>–



CaF<sub>2(s)</sub> system, the hygroscopicity of which significantly higher than in the initial components. Hygroscopicity of the lime after heat treatment in the mode of sintering of model charge was also evaluated and made 30.1 % during 336 h of soaking in the exiccator. This result has a good agreement with theoretical ratio of the molar masses of quicklime (CaO) and slaked lime (Ca(OH)<sub>2</sub>). The latter is higher of the first by 32.12 %.

Content of the free lime in the product can be approximately evaluated taking into account additivity of the hygroscopicity  $m_{\Sigma}$  of the sintered product of MgO<sub>(s)</sub>-CaF<sub>2(s)</sub> system as a result of contribution of all phases of this product and allowing that indicated sintered product has no other agents except for the initial chemical agents and products of reaction (1). For this it is also assumed that the hygroscopicities of fluorite  $m_f$  and manganese fluoride  $m_{MgF_2}$  are equal. Union of magnesite, fluorite and MgF<sub>2</sub> in the sintered product is considered as one agent the hygroscopicity  $m_0$  of which consists of contributions of magnesite  $m_m$  and fluorite  $m_f$  accepted considering their weight fractions in the initial charge:

$$m_0 = 0.65m_f + 0.35m_m = \\ = 0.65 \cdot 0.07 + 0.35 \cdot 0.21 = 0.119 \%$$

If hygroscopicity of the lime  $m_l$  is known than its mass fraction  $x_l$  in the sintered product of MgO<sub>(s)</sub>-CaF<sub>2(s)</sub> system can be easily determined from the following equation relatively to  $x_l$ :

$$m_{\Sigma} = x_l m_l + (1 - x_l) m_0. \quad (3)$$

The calculation using expression (3) showed that content of the free lime in the sintered product of MgO<sub>(s)</sub>-CaF<sub>2(s)</sub> system makes 4.47 wt.%.

Such minerals as alumina spinel MgO·Al<sub>2</sub>O<sub>3</sub>, calcium aluminate CaO·Al<sub>2</sub>O<sub>3</sub> and CaO·2Al<sub>2</sub>O<sub>3</sub> etc. are thermodynamically very stable compounds in a wide temperature interval. Therefore, increase of temperature provides beginning of their formation at achievement of sufficient diffusion mobility of the atoms of the initial components. Many factors (lattice defectiveness, presence of additions and moisture of constitution in the components, appearance of liquid and gas phases in salt-oxide systems) promote mineral formation under real conditions reducing temperature of beginning of the solid-phase reactions. For example, formation of spinel from commercially pure and naturally humid components becomes already apparent at 700–800 °C and that for forsterite makes 900 °C [10]. As a result the basic oxides and fluorite dominate over the acid oxides in the charge of sintered flux and the latter, probably, completely or mostly will be consumed for formation of complex oxides and oxyfluorides to the moment when the oxide system achieves its maximum temperature. On the contrary the fluorite and magnesite will remain in excess. The lime formed according to reaction (1) at temperature, approximately, 700–1000 °C, under these conditions reacts with, for example, Al<sub>2</sub>O<sub>3</sub> forming the calcium aluminates. However, after free Al<sub>2</sub>O<sub>3</sub> has been exhausted the lime, appearing during soaking at maxi-

imum temperature, cannot be quickly bound in the minerals.

Hygroscopicity of the high-basicity synthetic flux (see the Figure and Table 1) is reduced with the increase of temperature of sintering and duration of soaking at maximum temperature. Reduction of a content of the free lime due to processes of mutual dissolution of the components at high temperatures, as well as reaction of CaO with the initial chemical compounds with formation of more complex secondary minerals [10], can, probably, explain such dependence. However, speed of these processes, apparently, is not enough for complete binding of the lime, formed according to reaction (1). Therefore, increased hygroscopicity of the finished high-basicity synthetic flux of MgO-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is caused by remains of some amount of the free CaO.

## CONCLUSIONS

1. It was shown that hygroscopicity of the flux increases 10–23 times and become comparable with hygroscopicity of the agglomerated flux with rise of basicity of the synthetic flux from 0.8 to 2.4 times. The latter is provided by simultaneous rise of weight fractions of magnesite and fluorite in its composition.

2. It was determined that the presence of the free lime, forming as a result of chemical reaction between CaF<sub>2</sub> and MgO taking place in MgO-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at high (approximately 1100 °C) temperature and absence of the acid oxides in a free form which could effectively bound the lime in the minerals, in composition of the synthetic flux can be the reason of high hygroscopicity of the synthetic fluxes of MgO-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system.

3. It was stated that hygroscopicity of the high-basicity synthetic fluxes can be significantly increased by rise of sintering temperature and duration of soaking at this temperature. However, their hygroscopicity is significantly higher than in fused ones.

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