INFLUENCE OF TECHNOLOGICAL FACTORS IN MANUFACTURE OF LOW-HYDROGEN ELECTRODES ON HYDROGEN CONTENT IN THE DEPOSITED METAL

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PWI department of «Physico-chemical processes in the welding arc», led by Prof. I.K. Pokhodnya, academician of NASU, celebrated its 50th anniversary in 2012. Alongside the work on arc welding metallurgy and development of welding consumables, a considerable scope of research conducted by the department staff during this period deals with improvement of the technology of mechanized production of welding electrodes. This work enables clarifying the nature of the phenomena which are the basis for technological processes of manufacturing this kind of mass products, as well as improving the metallurgical, technological and service characteristics of electrodes and their quality. Given below are the results of investigation of the influence of such technological factors of manufacturing low-hydrogen electrodes as composition and amount of water glass in the electrode compound, its interaction with marble in the electrode coating, as well as organic hydrocolloids (carboxylmethyl cellulose and alginates) on dehydration of electrode coating and hydrogen content in the deposited metal. It is found that alkali hydrosilicates remaining in the electrode coating after dehydration of its water glass binder during electrode heat treatment, are a potential source of hydrogen in the deposited metal. There exists a direct relationship between water-retaining capacity of sodium-potassium hydrosilicates, dependent on the module and Na_2O:Ka_2O ratio, potential hydrogen content in the coating and hydrogen content in the deposited metal. However, at evaluation of the degree of potential hydrogen «assimilation» by the deposited metal, we should take into account the possible influence of potassium and sodium ions contained in the hydrosilicate, on fluorine removal from the reaction of hydrogen fluoride formation and on kinetic conditions of hydrogen sorption and desorption by electrode metal drop. Marble powder, contained in the electrode coating, and water glass which is the coating binder, interact with each other in a heterophase fashion. Calcium ions coming to the water glass binder lower the water-retaining capasity of alkali hydrosilicates. Products of interaction on marble particle surface hinder their thermal dissociation up to higher temperatures, compared to the temperature of pure calcite dissociation. Both promote lowering of hydrogen content in the deposited metal. Organic hydrocolloids such as sodium modifications of carboxylmethyl cellulose (CMC) and sodium or potassium alginates, are sorbed by the surface of marble particles and, blocking water glass access to it, they hinder the heterophase transition of calcium ions into the water glass. This has a favourable effect on the technological properties of electrode compounds, but at the same time improves the water-retaining capacity of alkali hydrosilicates in the electrode coating and hydrogen content in the deposited metal. Calcium ions are capable of moving from calcium-containing CMC modifications and alginates into the water glass binder as they do from calcite particle surface. Therefore, they should be considered as technological additives, which not only increase the plasticity of electrode compounds, but also lower the potential hydrogen content in the coating and hydrogen content in the deposited metal. 15 Ref., 8 Tables, 7 Figures.

Keywords: *manual arc welding, welding electrodes, electrode coating, water glass, hydrogen in the deposited metal, cold cracks, technological causes for hydrogen lowering*

Factors influencing hydrogen content in the deposited metal are conditionally subdivided into the metallurgical and technological ones. Metallurgical factors determine the thermodynamic and kinetic conditions of the process of hydrogen dissolution in the molten metal (hydrogen partial pressure in the arc atmosphere, its solubility in the metal and slag, temperature and size of specific surface separating the molten metal and water-containing gas or slag phase, duration of melt interaction with the environment, etc.). Technological factors characterize the intensity of sources of hydrogen coming to the welding zone and deposited metal and include potential content of hydrogen in the coating differentiated by the strength of the bond with coating materials, in particular in the form of:

- constitution moisture of mineral components;
- residual moisture of alkali silicate binder;
- remnants of organo-colloidal plastifying additives;

- moisture absorbed by the coating from air during electrode storage;
- atmospheric moisture penetrating into the arc zone from air.

In principle, they complement each other and should be considered jointly at assessment of the results of the deposited metal hydrogenation. Influence of technological factors becomes quite significant in the case of electrodes capable of ensuring hydrogen content below 5 ml/100 g of deposited metal, determined by mercury or chromatographic method.

The main source of hydrogen is dry residue of the binder consisting of alkali hydrosilicates with different degrees of dehydration. It and, to a certain extent, filler materials (organic, mineral ore components with constitution moisture, ferroalloys), fulfill this function, if hydrogen, initially present in their composition, is not removed from them at 400 °C temperature, used for baking low-hydrogen electrodes.

Water-retaining capacity of alkali hydrosilicates depends on chemical composition. They act as fire-retardants relative to organic ingredients. Ore-mineral components can slow down or accelerate alkali hydrosilicate dehydration, depending on their substantial and granular composition and on the degree to which the temperature range of their dehydration facilitates running of the reaction of polycondensation of silicon-oxygen anions of alkali hydrosilicates in the coating.

Water-retaining capacity of alkali hydrosilicates and hydrogen content in the deposited metal. Free moisture contained in water glasses (silicate solvent proper) evaporates at soaking in air (room temperature), and moisture associated with alkali hydrosilicate is preserved in the solidified residue. Part of it in the form of water molecules is coordinated in the hydration shell of alkali cations, and the other (in the form of hydroxyl groups) is part of the structure of silicon-oxygen anions (SOA). As temperature is increased both kinds of moisture are removed from alkali hydrosilicate, the first easier than the second. Therefore, at the temperature above 400 °C (right up to melting), predominantly SOA hydroxyl moisture remains in it.

Moisture removal from SOA structure occurs by polycondensation reaction, and moisture is considered to be not only its product, but also a catalyst. In terms of kinetics, the reaction proceeds faster, and the dehydration process is realized more completely, if the evolving moisture is not removed immediately from the material, but contacts the condensing anions for a certain time, participating in their regrouping. Its development is the more difficult, the more is the anion polymerized. Therefore, in highly polymerized SOA, for instance, of potassium, rubidium and cesium silicates, despite their higher permeability for water vapour removed during dehydration, more moisture remains, nonetheless, than in lithium and sodium hydrosilicates, subjected to the same heat treatment. This is confirmed by comparison of energies of dehydration activation of potassium and sodium hydrosilicates (Table 1), determined by us by processing the results of thermogravimetric analysis with the method described in [1]. Residual moisture of the coating made with application of such glasses, as well as with higher content of diffusible hydrogen in the deposited metal $[H]_{dif.d.m}$ also turns out to be higher (Table 2).

Increase of $[H]_{dif.\ d.m}$ content should be promoted, to a certain extent, by fluorine losses in the fused coating, caused by formation of alkali metal fluorides, the probability of which rises at transition from lithium to cesium glass.

Influence of modulus *M* on water-retaining capacity and residual moisture of sodium-potas-

Table 1. Thermokinetic characteristics of dehydration of sodium, potassium and sodium-potassium hydrosilicates

Kind of hydrosilicate	Dehydration indices	
	T_s, °C	E, kJ/mol
$Na_2O{\cdot}3.0SiO_2$	115	3.1
$Ka_2O{\cdot}3.2SiO_2$	140	10.0
$0.7Na_2O{\cdot}0.3K_2O{\cdot}2.7SiO_2$	125	4.4
$0.7Na_2O{\cdot}0.3K_2O{\cdot}2.9SiO_2$	95	1.5
$0.7Na_2O{\cdot}0.3K_2O{\cdot}3.0SiO_2$	120	2.5

Note. T_s and E are the temperature of maximum rate and activation energy of the dehydration process.

Table 2. Influence of the kind of water glass on coating moisture and hydrogen content in the deposited metal (glycerin method)

Kind of water glass	C_m, mol/100 g	W_T, wt.%	Weight fraction in deposited metal, %		$[H]_{dif}$, ml/100 g of deposited metal
			Mn	Si	
$Li_2O{\cdot}3.5SiO_2$	0.030	0.10	1.45	0.60	3.9
$Na_2O{\cdot}3.0SiO_2$	0.030	0.10	1.40	0.50	5.1
$K_2O{\cdot}3.0SiO_2$	0.030	0.30	1.40	0.40	6.1
$Cs_2O{\cdot}3.1SiO_2$	0.015	0.30	1.10	0.30	8.3

Note. C_m is the molar fraction of silicate in the coating; W_T is the residual moisture of the coating; $[H]_{dif}$ is the average value of the results of three parallel measurements.

sium hydrosilicates is also attributable to presence of two kinds of moisture contained in them. Fraction of moisture related to alkali cations, decreases with increase of modulus, whereas it grows in SOA structure. Resulting effect is described by an extremal curve, the minimum of which falls on the modulus approximately equal to 3.0 un. [2]. Minimum values of thermokinetic dehydration characteristics also correspond to it (see Table 1). $[H]_{dif.d.m}$ content should depend also on the fraction of dry residue of water glass in the coating, which usually decreases with modulus increase. Combined hydrosilicates of $0.7Na_2O{\cdot}0.3K_2O{\cdot}MSiO_2$ have lower water-retaining capacity than pure sodium or potassium analogs, as the reaction of their polycondensation proceeds more readily and completely than that of pure components of which they consist [2].

We attributed it to the increased probability in combined hydrosilicates of meeting of various SOA structural forms, which are located in the field of action of sodium and potassium cations, the polycondensation of which results in release of bound water.

The filler separates binder fragments in electrode coating, which participate in polycondensation reaction and, as a rule, hinders moisture removal from the coating at electrode baking. Moisture is present in the structure of many electrode compound fillers, the greater part of which is preserved at the temperature of low-hydrogen electrode baking. Nonetheless, at favourable combinations of dehydration ranges, evolution of this moisture can to some extent facilitate running of the reaction of polycondensation of alkali hydrosilicates [2].Constitution moisture of such alumosilicates, as mica-muscovite, kaoline and talc, remains in their structure after electrode baking and promotes an increase in $[H]_{dif.d.m}$ content. Synthetic mica, in the structure of which hydroxyl ions are replaced by fluorine during its pyrogenic synthesis, is an exception [3].

In view of the above, the concepts of the influence of water glass composition and dose on hydrogen content in the metal deposited with low-hydrogen electrodes can be precised, using the results of investigations derived in [4].

Test electrodes close by their coating composition to UONI-13/55 electrodes, were produced using sodium-potassium (M = 2.7–3.4 un.) and potassium-sodium (M = 2.7–3.1 un.) water glasses of different density (Table 3). Electrodes manufactured with application of sodium-potassium water glass and marked by C and D indices, were baked at 400 °C for 30, 60 and 120 min that enabled assessment of coating dehydration kinetics. Electrodes of A and B series made with application of potassium-sodium water glass, were baked at the same temperature for 30 and 120 min. W_T was assessed by heating a sample in an oxygen flow at 1100 °C (IIW method), and $[H]_{dif.d.m}$ — by glycerine method [4].

Weight fraction of W_T varied from 0.07 to 0.5 %, and $[H]_{dif.d.m}$ content was proportional to coating moisture, being within 2.6 to 12 ml/100 g of deposited metal. The interaction between $[H]_{dif.d.m}$ and W_T can be described by linear regression equations given in Table 3, judg-

Table 3. Composition, characteristics and weight fraction of water glass in test electrode coating

Electrode series and weight fraction of $Na_2O + K_2O$ in the coating, %	Kind of glass	Modulus, units	Density, g/cm^3	Weight fraction of water glass, %	$[H]_{dif.d.m} = f(W_T)$
A 3.10–3.60	Potassium-sodium	2.7	1.40	27	$[H]_{dif.d.m} = 1.08 + 18.60W_T$
		2.9			
		3.1			
B 3.30–3.80		2.9	1.36	30	$[H]_{dif.d.m} = 0.20 + 24.40W_T$
			1.40		
			1.44		
C 2.45–2.85	Sodium-potassium	2.7	1.40	27	$[H]_{dif.d.m} = 1.05 + 17.85W_T$
		3.1			
		3.4			
D 2.85–3.40		2.9	1.36	30	$[H]_{dif.d.m} = 1.30 + 21.10W_T$
			1.40		
			1.44		
			1.48		

ing by which $[H]_{dif.d.m} = f(W_T)$ straight lines differ from each other by their inclination to abscissa axis and are shifted along the vertical relative to each other. At the same coating moisture level (for instance, 0.2 %) hydrogen content varies from 4.80 to 6.40 ml/100 g of deposited metal, i.e. by 30 %. In the case of low hydrogen levels, such scatter should be regarded as quite significant.

In order to clarify its causes, we used the techniques described below. We will assume that all the moisture in the coating is concentrated in the residue of alkali hydrosilicate. With the change of composition and dose of water glass in the electrode coating the dose and degree of silicate hydration in the baked electrode coating, i.e. amount of moisture associated with it, changed at the same time. In physical chemistry moisture is calculated from dry substance and is presented in molar units as the quantity of water moles per one mole of dehydrated silicate, ϖ. Quantity of silicate moles in the coating is found as quotient of division of dry residue weight by its molecular mass. Quantity of H_2O moles is calculated as quotient of division of the mass of moisture preserved in the silicate, by molecular mass of water.

The data lacking in [4] (silicate dry residue and its molar moisture content, depending on the kind, modulus and density of water glasses) was calculated using formulas given in [5], having converted them by additivity rule, for combined water glasses:

$$\frac{1}{\rho - \rho_0} = \frac{\varpi + \omega_0}{b}, \qquad (1)$$

where ρ and ρ_0 is the density of water glass and solvent (equal to a unity for water); b and ω_0 are the constants additively dependent on the composition of alkali silicate; $b = 4.701 + 2.130M$; $\omega_0 = 1.109 = 1.537$ (sodium-potassium glasses); $b = 5.082 + 2.050M$; $\omega_0 = 0.750 + 1.780M$ (potassium-sodium glasses).

ϖ value calculated by formula (1) in sum with silicate molecular mass is the mass of water glass in the coating, and the fraction of silicate molecular mass in it is the dry residue of water glass. Knowing the dose of water glass in the electrode compound, weight fraction of silicate (dry residue) in the coating was calculated. It remains in the coating as the coating is dehydrated during electrode baking without changes in the mass and mole units. Only W_T determined during experiments decreases [4].

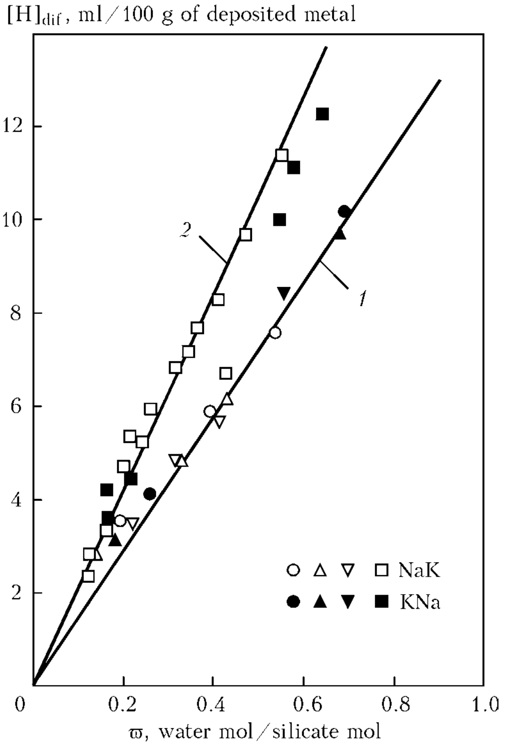

Figure 1. Interrelation of hydrogen content in the deposited metal and moisture content of sodium-potassium and potassium-sodium hydrosilicates in test electrode coating: *1* — ρ = const (27 % glass); *2* — M = const (30 % glass)

Figure 1 gives dependence of $[H]_{dif.d.m}$ content on molar moisture content of hydrosilicate in the coating of electrodes baked during selected time intervals at 400 °C, which was derived as a result of our calculations. It is seen that with such an interpretation the experimental results are quite clearly stratified into two groups. It each group they are approximated by straight lines, starting from the origin of coordinates, which differ from each other only by the angle of inclination to ϖ axis. The lower straight line belongs to electrodes of A and C series, in which the glass modulus was changed. Upper curve 2 belongs to electrodes of B and D series with M = 2.9 un., and varying density. At the same ϖ value electrodes of B and D series provide higher $[H]_{dif.d.m}$ content than electrodes of A series. This can be explained as follows.

Electrodes, the application of which provides higher $[H]_{dif.d.m}$ content, also have a higher fraction of alkali oxides in the coating. Reaction of formation of alkali metal fluorides should neutralize part of active fluorine and, thus, weaken its role in lowering of partial pressure of hydrogen by binding it into hydrogen fluoride.

Stabilizing action of potassium and sodium on the arc discharge can cause expansion of the arc column (and of fraction of the surface of that part of the drop through which hydrogen absorption from the arc atmosphere occurs). Increase of the ratio of surface areas, through one of which hydrogen absorption from the plasma by the electric arc takes place, and through the other, located outside the active spot, hydrogen evolves simultaneously from molten metal, is an important kinetic characteristic of the process of setting of final concentration of diatomic gases in the deposited metal [6]. Influence of this factor is similar to reduction of concentration of fluorine binding hydrogen in the arc atmosphere.

Figure 2 gives the results of assessment of dehydration kinetics in coatings of electrodes of C series, made with sodium-potassium water glass with different modulus values. It is seen that dehydration of electrode coatings really proceeds very slowly. Molar moisture content of the coating decreases, becoming close to equilibrium value for 400 °C temperature only after 2 h soaking of electrodes made with water glass with $M = 3.3$ un. (temperature curve of dehydration comes to a horizontal section). Equilibrium moisture content of coatings of two other studied variants of electrodes from this series is not achieved. The lowest moisture content (0.14 %) was obtained in a coating made with water glass with the modulus of 3.1 un. In coatings made with water glass with the modulus of 2.7 and 3.3 un., it is approximately 1.5 times higher at 0.18 and 0.22 water mol/silicate mol, respectively. It is important that hydrogen content in the metal deposited with the same electrodes, changes in proportion to coating moisture content, being equal to 3.3, 2.6 and 3.1 ml/100 g of deposited metal, for moduli of 2.7, 3.1 and 3.3 un., respectively.

In other words, residual moisture of sodium-potassium hydrosilicate changes, depending on the modulus value by an extremal law, both in the free state and in the electrode coating composition. $[H]_{dif.d.m}$ also changes in an extremal fashion, accordingly, although in this experimental series, part of fluorine removed by alkali from the reaction of formation of hydrogen fluoride was the greater, the lower the water glass modulus.

No such relationship of $[H]_{dif.d.m}$ content and final moisture level of hydrosilicate in the coating was established for electrodes of A series.

Therefore, when searching for methods to lower $[H]_{dif.d.m}$ content, alongside the residual moisture of the coating, the concurrent factors influencing hydrogen partial pressure in the arc atmosphere should be taken into account.

Influence of marble interaction with water glass in the coating on hydrogen content in the deposited metal. From the very start of mastering full-scale low-hydrogen electrode production by the press method, their manufacturers had to deal with unsatisfactory technological properties of electrode compounds and assumed that this is caused by chemical interaction of marble with water glass by the following exchange reaction:

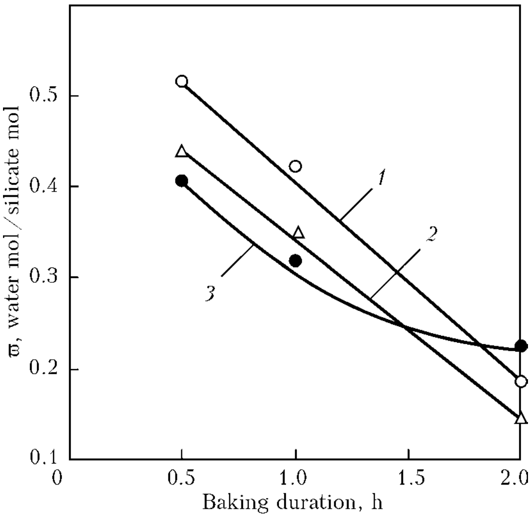

Figure 2. Kinetics of dehydration of low-hydrogen electrode coating at the temperature of 400 °C, made with application of sodium-potassium glass with modulus of 2.7 (*1*); 3.1 (*2*); 3.3 (*3*) units

$$\begin{aligned} &Na_2O{\cdot}M SiO_2 + CaCO_3 = \\ &= Na_2CO_3 + (M - 1)SiO_2 + CaSiO_3. \end{aligned} \qquad (2)$$

The validity of such an assumption was called into question [7], however, it was not possible to establish the real cause of this phenomenon for many years.

We have found out that marble indeed interacts with water glass, but by a much more complex mechanism. Calcium from marble (similar to other calcium-containing minerals difficult-to-dissolve in water) dissolves in water glass and is capable of causing its curing in the process [8].

In physical chemistry the mechanism of such curing is considered in terms of heterophase interaction, as the reaction proceeds between the solid substance and water solution of inorganic polymer. Products responsible for curing of the system, can form only after completion of the slow, i.e. quite prolonged incubation period, during which calcium concentration in water glass will reach oversaturation, sufficient for nucleation of new hydrosilicate phases, amorphous as to their structure [9].

The above-mentioned period includes chemisorption [10] and ion-exchange stages. Silicon-oxygen anions of alkali hydrosilicates, which are present in water glass, absorbing calcium ions in exchange for hydroxyl ions, act as cationite [11]. Calcium which has passed into solution during the incubation stage forms intermediate compounds with silicate ions on ≡Si–O–Ca–O–Si≡ binders. They become the new phase nuclei. Hy-

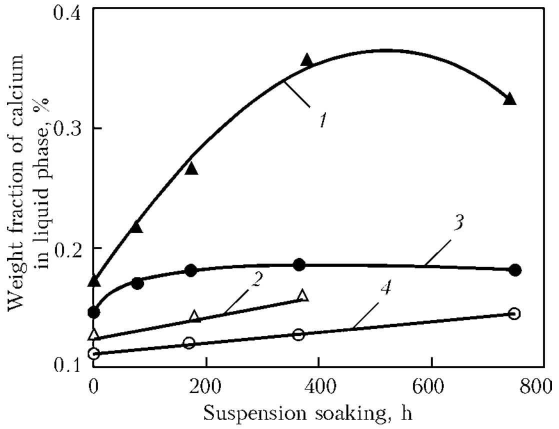

Figure 3. Kinetics of calcium transition from marble powder into water glass (weight fraction in suspension is 25 %): *1*, *3* — modulus of 2.6 units, viscosity of 400 (*1*) and 50 MPa·s (*3*); *2*, *4* — modulus of 3.6 units, viscosity of 330 (*2*) and 50 MPa·s (*4*)

droxyl ions are released from alkali hydrosilicates with free moisture formation.

Activity of natural calcium carbonates in water glass compositions depends on their structure formed during prolonged geological periods. Quarry chalk is an inert material in relation to water glass. Marble is more active than limestone, although its activity is lower than that observed in calcium silicates, which make up the basis of silicate cements. Even more active is natural aragonite having a denser hexagonal structural cell, unlike the cubic cell, characteristic for the structure of other above-mentioned kinds of calcites. Aragonite structure forms also at fine grinding of marble [12]. Together with amorphization of particle surface and energy, accumulated by them during grinding, it becomes the cause for increased chemical activity of fresh refined marble powders. Natural seasoning for 7 to 10 days partially phlegmatizes them. However, the activity, which is directly related to appearance of aragonite, can be suppressed only by powder heating up to 400 °C.

Calcium solubility in water glass at the moment of oversaturation, does not depend on the nature of the mineral, from which is comes to water glass. When recalculated to calcium weight fraction for sodium glasses it varies from 0.6 up to 1.3 %, growing within these ranges at modulus lowering from 3.3 to 2.6 units and increase of alkali silicate concentration in water glass right up to 5–6 moles of SiO_2/l [9]. Mineral nature and its particle dispersity influence only the calcium dissolution rate.

Analyzing the above-said, it may be assumed that electrode compositions should react to running of the incubation period of marble interaction with water glass, at the end of which new hardening phases are formed due to:

- more intensive improvement of raw (plastic) strength compared to coatings, not having calcium-containing minerals in their composition and this, indubitably, should be accompanied by deterioration of their plasticity;
- additional release of moisture from the structure of alkali hydrosilicates and lowering of potential content of hydrogen in the coating after electrode heat treatment;
- changes of surface structure of marble particles participating in the reaction, that may result in the change of kinetic indices of their thermal dissociation during electrode heating and melting.

During experiment performance we observed hardening of electrode compounds under the impact of calcium transition into water glass [13]. Role of the last two factors in regulation of $[H]_{dif.d.m}$ content was revealed by us during investigations, the results of which are given below.

Calcium from marble dissolves in sodium-potassium water glass to a somewhat smaller extent, than in sodium glass. For instance, limit solubility of calcium in low-modulus sodium-potassium glass, is equal to 0.20 and 0.55 wt.% at SiO_2 concentration of 5.85 and 6.35 mol/l, respectively. It is even lower in high-modulus glass and is not higher than 0.15 wt.% at SiO_2 equal to 5–6 mol/l. As follows from Figure 3, it grows with viscosity increase and lowering of water glass modulus. Calcium transition during the incubation period is accompanied by improvement of water glass viscosity. The effect is the more pronounced, the higher its initial viscosity (Figure 4).

Incubation period is over at the moment of achievement of maximum concentration of calcium in the solution and viscosity of water glass. Both the indices decrease with the start of new phase precipitation and will not be restored as long as the new phase precipitates.

Rate of calcium dissolution rises, when freshly ground marble is used. So, at the same duration of marble powder mixing with water glass, calcium transition decreases from 0.25 wt.% (freshly ground marble) to 0.15 wt.% (same powder soaked in air for 15 days). Increasing calcium transition is promoted by application of intensive modes of powder mixing with water glass or increasing marble particle dispersity.

Influence of calcium impurity on water-retaining capacity of alkali hydrosilicates was studied by derivatography method [2].

Samples of sodium-potassium hydrosilicates (modulus of 2.80; 3.05; and 3.30 un.) with calcium content not exceeding its limit solubility, were prepared. For this purpose a saturated water solution of calcium hydrate oxide $Ca(OH)_2$ in the amount from 0.05 up to 0.20 wt.% was added to water glasses, in order to obtain the pre-specified molar concentration of calcium in the solution in the range from 2.5 up to 12 mmol Ca/mol SiO_2. Samples for comparison were hydrosilicates without calcium. During water glasses mixing with $Ca(OH)_2$ solution, colloidal lime precipitated, which, being gradually compressed in its volume through syneresis, rejected the solvent. Slow evaporation was used to bring all the samples to solidlike state (with moisture content of 20–35 wt.%). Then thermogravimetric analysis (TGA) method was used to find in each of them the share of moisture remaining after hydrosilicate heating up to 400 °C. Figure 5 gives the results of experiments.

It is seen that calcium ions Ca^{2+} indeed influence water-retaining capacity of alkali hydrosilicates. At water glass moduli of 2.80 and 3.05 units small Ca^{2+} additives lower hydrosilicate residual moisture content (effect similar to mixed alkaline one, observed in combined sodium-potassium silicates, but Ca^{2+} action is manifested at concentrations by three orders of magnitude smaller than the concentration of accompanying alkali cation). At concentrations, exceeding the optimum ones, calcium causes an opposite effect, and water-retaining capacity of hydrosilicate rises. In the real electrode compounds Ca^{2+} concentrations can, apparently, be both greater and smaller than the found optimum. Hence the unpredictability of the induced result as regards the achieved degrees of coating dehydration.

At water glass modulus of 3.30 units the dissolved calcium monotonically increases the hydrosilicate water-retaining capacity in the entire range of its obtained concentrations.

It is important to note that at molar concentrations exceeding 7.5 mmol Ca/mol SiO_2, the value of alkali silicate modulus no longer influences its water-retaining capacity. The role of dissolved calcium in ensuring the residual moisture content of alkali hydrosilicates becomes the determinant one here.

Investigation of water vapour mass-spectra in the gas phase over the heated samples of hydrosilicates showed that intensive dehydration of hydrosilicates under calcium influence gradually shifts to the region of ever higher temperatures, thus confirming that ever greater amount of bound moisture remains in the hydrosilicate, baked at 400 °C.

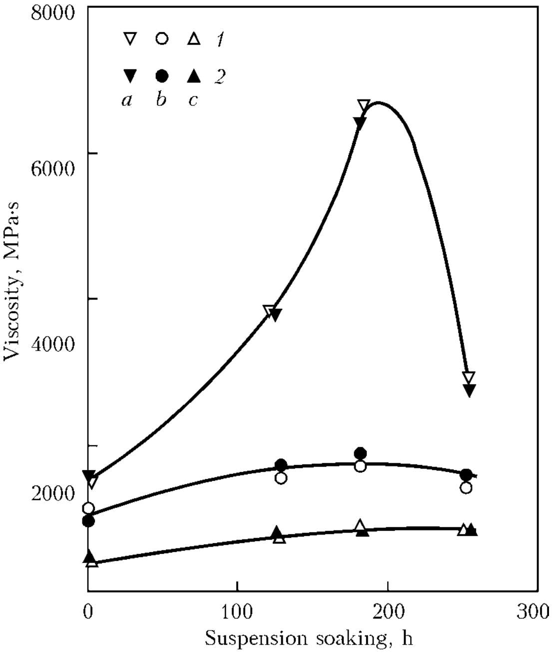

Figure 4. Change of viscosity of marble suspensions in sodium-potassium glass with modulus of 2.87 (*1*) and 3.11 units (*2*) in time. Initial viscosity of water glass is 1800 (*a*), 1000 (*b*) and 500 (*c*) MPa·s [13]

So, at weight fraction of calcium in water glass, %: 0; 0.11; 0.22; 0.43 $[H]_{dif}$ content, ml/100 g of deposited metal is as follows: 4.6; 3.7; 3.0; 3.6, respectively. Here and further on $[H]_{dif}$ value was calculated as the average value of three parallel measurements, made by chromatographic method by A.P. Paltsevich, Cand. of Sci. (Eng.).

It was noted above that calcium transition from marble powder into water glass increases with increase of its dispersity. Data given in Ta-

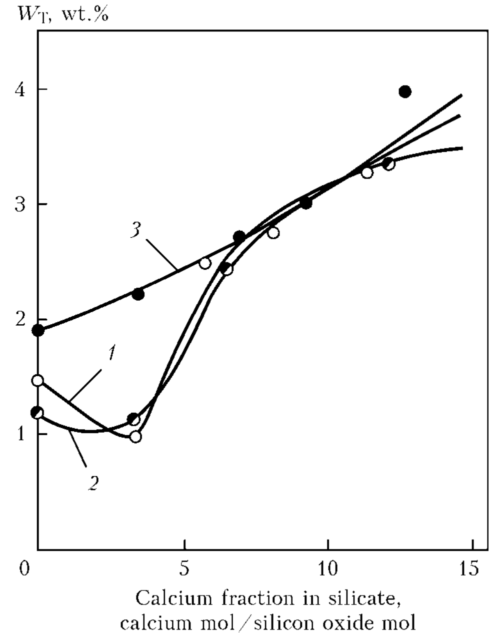

Figure 5. Influence of Ca^{2+} ions on water-retaining capacity of sodium-potassium hydrosilicates with modulus of 2.80 (*1*): 3.05 (*2*); 3.30 (*3*) units [13]

Table 4. Influence of charge dispersity on composition and content of hydrogen in the deposited metal

Weight fraction of −0063 particle size in the charge, %	Weight fraction in deposited metal, %		$[H]_{dif}$, ml/100 g of deposited metal
	Mn	Si	
0	0.51	0.14	3.3
20	0.71	0.30	3.4
40	0.65	0.37	3.1
60	0.54	0.29	2.8
80	0.47	0.24	2.5

ble 4, confirm that hydrogen content in the deposited metal also decreases in this case.

The following experiments and their results are a convincing proof of the fact that $[H]_{dif.d.m}$ decrease is related exactly to calcium transition into water glass. In the coating of test electrodes UONI-13/55 the content of Trilon B (komplexon) was gradually increased up to 0.12 wt.%. Trilon is disodium salt of ethylenediaminetetraacetic acid, which is usually used for absorption of calcium ions at water softening. Unlike ion-exchange resins (ionites) it is capable of removing calcium ions not only from water, but also from solutions containing the concurrent potassium and sodium ions. Adding komplexon to coating compound during charge mixing with water glass, we remove calcium from the solution. Here, water-retaining capacity of calcium-pure alkali hydrosilicate in the coating is restored and $[H]_{dif.d.m}$ content is increased. At increase of komplexon weight fraction, %: 0; 0.04; 0.08; 0.12, $[H]_{dif}$ content, ml/100 g in the deposited metal changes as follows: 4.6; 5.8; 5.3; 6.7, respectively.

Effect similar to the one obtained with komplexon, is anticipated at application of potassium oxalate [8]. Comparison of effects due to calcium spontaneously moving into the solution from marble, on the one hand, and calcium, deliberately added to the compound in the form of volumetric solution of calcium chloride $CaCl_2$, on the other hand, revealed that the above calcium sources are to some extent antagonistic in water glass. When coarse-grained charge is used, and the anticipated transition of calcium into the solution from marble is minimum, adding $CaCl_2$ solution to the compound turns out to be quite effective in terms of lowering $[H]_{dif.d.m}$ content. Contrarily, at application of fine-grained charge, when the anticipated coming of calcium into the solution from marble is maximum, adding $CaCl_2$ to the compound is no longer effective.

Proceeding from the results of these experiments, we came to the conclusion that marble should be regarded not only as a source of calcium, which allows adjustment of water-retaining capacity of alkali hydrosilicate, but also as coating ingredient, the gas-forming capacity of which, essentially lowering partial pressure of hydrogen in the arc atmosphere, rises at its heterophase interaction with water glass for a reason not clear so far.

This can be assessed by comparing the process of thermal dissociation of marble powder in the pure form and in compositions with water glass. Powders of marble from Koelgin field were studied, in particular in a mixture with sodium-potassium silicate block in the amount of 13 wt.% or with fluorspar powder, taken in the molar ratio of $CaCO_3:CaF_2 = 1:1$. Coarseness of ingredient particles did not exceed 0.25 μm.

A sample of a mixture of marble powder with sodium-potassium water glass (M = 2.7 units, 22 % weight fraction in the mixture, 8 % recalculated to dry residue) brought to air-dry state, was studied separately.

Total pattern of thermal dissociation of powderlike marble at proportional heating is in good agreement with the published data of other authors. Its dissociation starts at the temperature of 650 °C, maximum rate of thermal dissociation reaction is found at 890 °C, and the process is over at 940–950 °C. Losses of sample mass are very close to theoretical content of carbon dioxide gas CO_2 in marble and are equal to 43.2 % (44 % in pure calcium carbonate $CaCO_3$).

In mixtures with fluorite and with silicate block the running of marble dissociation almost does not change. The revealed very slight differences are in agreement with published data, in which the facilitating influence of additives in the form of alkali oxides and fluorides on calcium decomposition is noted. The found thermoeffects behind the decarbonization peak are caused by the reaction of ordering of the formed metastable oxide.

Sample mass losses recalculated by the method of [1] and graphically presented in Figure 6, show that the seeming energy of activation of the process of thermal dissociation of marble for all the three variants of the studied dry mixtures remains constant (experimental points fall on the same curve). Apparently, in all these cases the rate of calcium dissociation is limited not so much by its initial stage, dependent, primarily, on the condition of its grain surface, but also by subsequent stages of the process, on which the studied additives cannot have any influence.

Water glass turned out to be an additive, which essentially affects the activation energy of the process of marble dissociation. We mean not the threshold stage or the characteristic temperature T_s, which are hidden from direct observation by effects accompanying the alkali silicate dehydration proceeding at this moment of time, but the main stage, during which CO_2 is actively released. As follows from Figure 6, starting from 720 °C this stage becomes the dominating one in its influence on reduction of sample weight, caused by CO_2 release and runs with greater energy impediments than in hydrosilicate absence. Below this temperature the sample mass losses are, apparently, determined predominantly by dehydration of hydrosilicate binder, and if its energy is assessed by the inclination of the respective section of the straight line, than it can be assumed that its running is more difficult than carbonate dissociation in the absence of hydrosilicate film on its particle surface.

The following designations are used in Figure 6: G_0, G_t, and G are the initial, final and current mass of the sample; $\theta = T - T_s$, where T and T_s are the current temperature and temperature of maximum rate of dissociation reaction.

Considering that dehydration of silicate binder, coating $CaCO_3$ grains, which involves high energy consumption, goes on also above 720 °C, its inhibitory action on carbonate dissociation under the conditions of high-rate proportional heating can be quite substantial (reports of positive role of water vapours in realization of calcite dissociation are related to long-term isothermal variants of heating [14]).

Another possible cause of inhibitory action of hydrosilicate film on thermal dissociation of calcium carbonate can be the consequences of interaction of its particle surface with water glass at the stage of electrode compound preparation. Judging by the concentration of calcium ions detected by chemical analyses in water glass, and by the results of calculation estimates, up to 10 elementary surface layers of calcite grains could become involved in the dissolution process. This results in a kind of their phlegmatization, i.e. delayed reaction to the initial heating phase.

Recently published investigation results [15] on the whole confirm our conclusions that application of finely-dispersed marble in the coating of low-hydrogen electrodes promotes lowering of $[H]_{dif.d.m}$ content. Experiments were conducted with electrodes, in the coating composition of which marble with regular grain composition (31 wt.%) was gradually replaced by marble powder, consisting of nanosized particles. As a result of such a replacement $[H]_{dif.d.m}$ content decreased from 3.8 to 2.45 ml/100 g of deposited metal at 50 % replacement and down to 2.3 ml/100 g of deposited metal at complete replacement of regular marble by its nanosized analog. The authors of the work explained this phenomenon by lowering of hydrogen partial pressure in the arc atmosphere caused by more intensive evolution of CO_2 from the surface of nanosized $CaCO_3$ particles. Judging by the deposited metal composition, oxidizing potential of the arc atmosphere remained unchanged. From our point of view, lowering of $[H]_{dif.d.m}$ content occurring under the influence of finely-dispersed marble powders in the coating (including also nanosized modifications), is caused by the processes of their heterophase interaction with water glass, which lead to reduction of potential content of hydrogen in the coating and its partial pressure in the arc atmosphere.

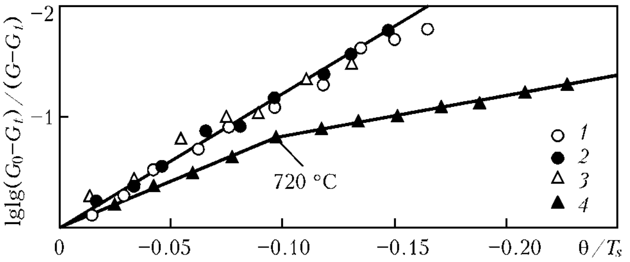

Figure 6. Dependence of the change of sample weight on reduced temperature in the coordinates of Gorovits–Mettinger equation [1]: *1* — marble; *2–4* — mixture of marble with silicate block, with fluorite, and with water glass, respectively

Role of organic hydrocolloids in regulation of hydrogen content in the deposited metal. Traditionally such organic hydrocolloids as carboxymethylcellulose (CMC) and alginates were regarded only as technological additive, effectively plastifying the electrode compound. After that at the stage of compound preparation and application on the rods it is «burnt out» of the coating during electrode heat treatment. In the case of Na-CMC, one can see that coating moisture found by IIW method in electrodes made with application and without application of Na-CMC, is indeed homogenized by value (Table 5) after their baking at the temperature of 400 °C.

At the same time, it is experimentally established that hydrogen content in the metal, deposited by electrodes initially containing Na-CMC in their coating, often is higher than for electrodes which were manufactured without CMC application (Table 6). Here $[H]_{dif.d.m}$ content changes much less than the initial CMC content in the coating.

We can assume that organic hydrocolloids with a non-symmetrical molecule structure, can

Table 5. Depth of dehydration of low-hydrogen electrode coatings during their baking

Electrode baking temperature, °C	Coating moisture, W_T, %		$\Delta W_T = W_T(A) - W_T(B)$, %
	A	B	
20	4.67	6.08	1.41
290	0.71	0.93	0.22
325	0.48	0.63	0.15
360	0.30	0.34	0.03
405	0.23	0.24	0.01

Note. Coating with A index — without CMC content, with B index — CMC content of 1.5 %.

be sorbed by the surface of marble solid particles similar to, for instance, salts of fatty acids in flotation processes, that allows suppressing calcium dissolution in water glass.

This is confirmed by the nature of IR-spectra of marble powders, contacting the water glass, after their pre-treatment by water solutions, as well as by water-glass Na-CMC dispersions. Na-CMC concentration in the dispersions is 2 %. Marble powder was sifted through a sieve with 63 μm cell size. Weight ratio of powder and liquid is 1:5. Sodium-potassium water glass with 2.9 un. modulus and 1000 MPa·s viscosity was used. Experiments were performed by V.G. Vojtkevich, Cand. of Sci. (Phys-Math.) and E.E. Fedorina, Eng.

CMC chemical and molecular composition was varied in broad ranges. In addition to Na-CMC with extreme values of substitution degree (SD) (from 65 to 130) and polymerization degree (PD) (from 350 to 1300), calcium CMC (Ca-CMC) was also used.

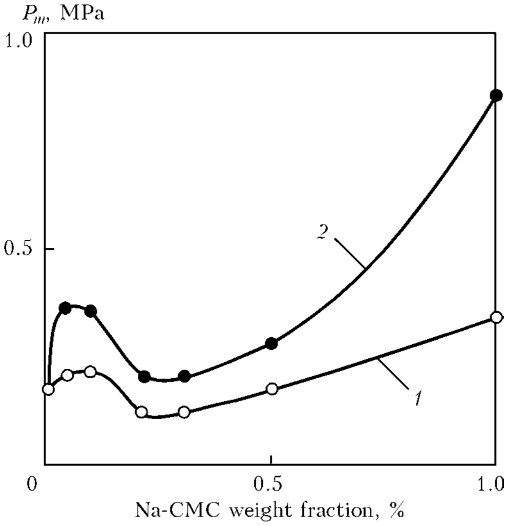

Figure 7. Influence of Na-CMC with different molecular composition on plastic strength of UONI-13/55 electrode compound: *1* — CMC 68/350; *2* — CMC 68/920

Marble powder interacted with the above-mentioned preparations for 30 min at periodical shaking of the suspension. Then it was separated by decantation from excess liquid phase, rinsed several times with water, and after 5 hour drying at 105 °C was studied on IR-spectra in the mode of incomplete compensation [9].

It is established that the adsorption pattern which is observed on the surface of marble particles treated by pure water glass, coincides with that which is described in [9]. Na-CMC, irrespective of SD and PD, being present in water glass, suppresses water glass sorption on calcite surface. Reflections in IR-spectra caused by out-of-plane deformation vibrations of carbonite anion under the influence of CMC return to their normal state (880 cm^{-1}), and the silica gel band at 1069 cm^{-1} disappears completely. Bands characteristic for adsorbed CMC gel appear instead of it.

So, presence of a blurred band in 1300–1100 cm^{-1} region, observed after marble powder treatment by Na-CMC water solution and its dispersions in water glass, can be due to transoriented methyl groups of sorbed CMC which either oust water glass SOA from the sorbent surface, or prevent their sorption. The thus blocked calcite surface naturally loses its capacity to supply calcium ions into water glass. In addition to that, the influence of water glass on the structure of calcium carbonate particle surface, on the condition of which the nature of their dissociation at heating depends, is weakened.

As hydrocolloids are in a powderlike form in the dry mixture, phlegmatization of the surface of marble particles during electrode compound preparation proceeds by not such an ideal mechanism. Before the hydrocolloid particles, while absorbing moisture from water glass, acquire the capacity of blocking the surface of marble grains,

Table 6. Hydrogen content in the metal, deposited with UONI 13/55 electrodes with organic additives in the coating, depending on their baking duration at the temperature of 400 °C

Additive kind and grade	Additive weight fraction, %	Glass weight fraction, %	$[H]_{dif}$, ml/100 g of deposited metal at baking duration of, h		
			0.5	1.0	2.0
Without additive	–	24	7.1	6.3	5.2
Na-CMC, Cecol DVY	1.0	25	11.5	11.6	11.8
	1.5		15.5	11.3	10.8
	2.0		14.6	12.9	12.2
Ca alginate, C/YSF	1.5	24	5.4	5.6	2.8
	2.0	25	5.4	5.2	4.4

a certain part of calcium has enough time to dissolve in water glass and influence $[H]_{\text{dif.d.m}}$ content. This is, in particular, confirmed by the results of experiments with komplexon.

The opposition of alkali silicate and Na-CMC in their tendency to take some place in the sorbed layer on the surface of calcite grains can be assessed by non-linear variation of plastic strength of UONI-13/55 coating at gradual increase of its content of powderlike CMC from 0 up to 1 % (Figure 7).

Low-viscosity (68/352) and high-viscosity (68/920) Na-CMC and sodium-potassium water glass with modulus of 2.9 units and viscosity of 0.175 Pa·s, which is readily sorbed by marble and dissolves calcium, were used. Water glass weight fraction was 22.5 %.

As follows from Figure 7, plastic strength of electrode compound P_m, which is equal to 0.19 MPa in the initial condition, first rises and then, having reached a small maximum, it is minimized at CMC content of 0.2–0.3 %. And only after that it continues monotonically growing exponentially at further increase of CMC content right up to 1 % (result caused predominantly by swelling of CMC particles through water glass moisture absorption by them). CMC molecular composition almost does not affect the position of extreme points along the concentration axis, but the high-viscosity preparation (68/920), on the one hand ensures greater P_m value, in particular in the maximum point, and, on the other hand, leads to a higher rate of its initial and post-minimal rise. Supposedly, P_m maximums are achieved, when the structuring impact of CMC and calcium ions is equalized by value, and the minimums are reached, when CMC absorption suppresses calcium transition from marble into the solution.

In the case of Ca-CMC application, IR-spectra bands in the region of 1300–1100 cm^{-1} are not observed. Silica gel bands are preserved, even though in a weakened form. Both of them are attributable to hindered adsorption of carbomethyl radicals of Ca-CMC on calcite particle surface. Apparently, strongly cross-linked by calcium ions, the above radicals have a more ramified structure, which is difficult-to-sorb by calcite surface, and, therefore, is not capable of reliably shielding it from direct contact with water glass.

It can be anticipated that in this case water-retaining capacity of alkali hydrosilicate should be influenced by calcium coming to it both from marble (not blocked by hydrpocolloid from contact with water glass), and from the hydrocolloid proper. Ca-CMC modification formed as a result of its interaction with alkali cation, should have a plastifying impact on the electrode compound.

In addition to that, delayed dissociation of marble particles, the surface of which is «phlegmatized» by adsorbed alkali silicate, should influence lowering of partial content of hydrogen in the arc atmosphere.

In other words, calcium form of organic hydrocolloids should be regarded not only as plasticizing (structure-forming) additive to electrode compound, but also as a quite effective means of lowering hydrogen content in the metal, deposited with low-hydrogen electrodes.

This is confirmed by the data given in Table 6, which were obtained when using calcium alginate — a hydrocolloid, which unlike Ca-CMC, is made from alginic acid — a product of processing sea weed.

Conclusions

1. Alkali hydrosilicates remaining in electrode compound after dehydration of water glass binder during electrode heat treatment, are a potential source of hydrogen in the deposited metal. There exists a direct relationship between water-retaining capacity of sodium-potassium hydrosilicates, dependent on modulus value and Na_2O:Ka_2O ratio, potential hydrogen content in the coating and hydrogen content in the deposited metal. However, at assessment of the degree of potential hydrogen «assimilation» by the deposited metal the possible influence of potassium and sodium ions contained in the hydrosilicate on fluorine removal from the reaction of hydrogen fluoride formation and on kinetic conditions of hydrogen sorption and desorption by an electrode metal drop, should be taken into account.

2. Marble powder, contained in the electrode coating, and water glass which is the coating binder, interact with each other in a heterophase fashion. Calcium ions coming to water glass binder, lower the water-retaining capacity of alkali hydrosilicates. Products of interaction on marble particle surface delay their thermal dissociation till higher temperatures, compared to that of pure calcite dissociation. The impact of these factors results in lowering of hydrogen content in the deposited metal.

3. Organic hydrocolloids such as sodium modification of CMC and alginates, are sorbed by marble particle surface, blocking water glass access to it, and transition of calcium ions into it. This has a favourable influence on the technological properties of electrode compounds, but enhances the water-retaining capacity of alkali

hydrosilicates in the electrode coating, and hydrogen content in the deposited metal. Calcium-containing modifications of CMC and alginates, from which calcium ions can go into the water glass binder, as they do from calcite particle surface, are technological additives, which not only increase electrode compound viscosity, but also lower the potential content of hydrogen in the coating and hydrogen content in the deposited metal.

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