The properties of electrode polarization, which take place at the boundary of liquid ferrosilicon with fused silicates, were examined in previous articles [1]. Here the absence of limiting current densities and the large values of the polarization were considered as an argument against diffusion inhibition, and the very small decay was taken as an argument against a retarded discharge. A hypothesis was presented that the polarization is caused by a retarded deformation and orientation of complex silicate ions in an electric field.

Naturally, this hypothesis requires additional verification. In particular, if it is correct, then the polarization should be practically independent of the electrode material. The following experiments, in which the ferrosilicon electrodes were replaced by ferrophosphorus electrodes (23% P), were conducted in order to prove this hypothesis.

The electrolyte was a silicate which contains 43% SiO_2, 46% CaO, 10% MgO, and a small amount of phosphides. The electrolyte was prepared by melting the carefully mixed oxide powders in a graphite crucible. Then a small portion of phosphorus pentoxide was added. The P_2O_5 deoxidized violently, and only a small part of the P_2O_5 remained in the melt, evidently in the form of phosphides [2]. After cooling, the silicate was crushed and

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* Numbers in the margin indicate pagination of original foreign text.

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placed in the electrolyzer. The electrolyzer construction and the method of measuring the polarization were the same as in the previous article [1].

The polarization curves, which were obtained at various temperatures, are given in Figure 1. For comparison, Figure 2 shows the corresponding results for ferrosilicon electrodes (22.5% Si) and an electrolyte consisting of 30% SiO_2, 50% CaO, and 10% MgO.* As can be seen from these figures, the cathode side of both electrodes remains linear ($\eta = ki$) up to significant polarizations. Although the magnitude of the proportionality coefficients (k) is larger for the ferrophosphorus electrodes than for the ferrosilicon electrodes, the activation energies, determined from the temperature dependence of k (Figure 3), are practically the same (115 kcal).

The anode sides for the ferrophosphorus electrodes start to curve at much smaller polarizations. Probably this curvature is caused by the higher temperatures (1560 to 1580° C) for the ferrophosphorus electrodes as compared to the temperatures (1440 to 1500° C) for the ferrosilicon electrodes. In some cases, a limiting instability of the anode polarization was observed for ferrophosphorus electrodes. This instability is possibly caused by the evolution of CO, which is formed by accidental contact between the electrolyte and the graphite leads. The gas evolution disturbs the electrolyte, destroys the orientation of the complex ions in the electric field, and sharply reduces the polarization.

However, this fact can also be interpreted as a proof of the concentrational dependence of the polarization. In this respect,

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* In Figure 4 of the previous article [1], the current density i is erroneously shown 2.4 times too large.

another possible origin of the polarization should be considered, which was not considered previously [1].
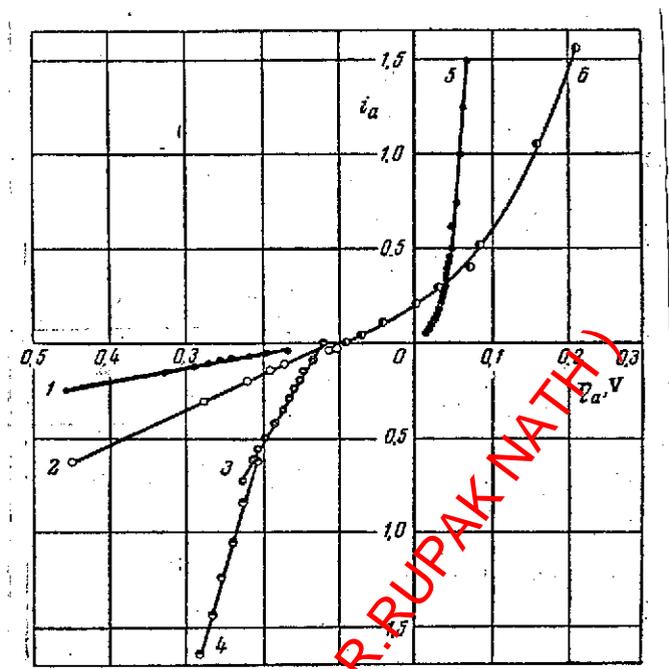

Figure 1. Polarization curves for phosphorus electrodes (23% P) and an electrolyte consisting of 43% SiO_2, 46% CaO, 10% MgO, and phosphides. The cathode lines 1, 2, 3, and 4 correspond to 1490, 1540, 1600, and 1610° C. The anode curves 5 and 6 correspond to 1560 and 1580° C

Experiment [3, 4] shows that slags containing a significant /375
concentration of bivalent silicon (SiO) along with a large percentage of silica are formed in the strongly reducing medium in industrial furnaces at high temperatures. Thus the possibility of electrochemical formation of bivalent silicon cannot be excluded in our experiments. Preliminary processing of the electrolyte by small currents was possibly insufficient for reaching an equilibrium concentration of SiO. In this case, the SiO-forming processes at the electrodes were dominating. If we neglect the form of the ions in the melt, then these processes can be represented by the equations

$$Si^{4+} + 2e^- = Si^{2+}; \qquad (1)$$

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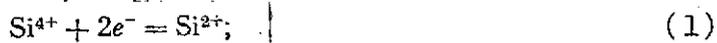
at either cathode, and by

$$Si - 2e^- = Si^{2+}.$$
(2)

at the anode containing silicon.

Experiments on the electrochemical formation of subcompounds of aluminum and sodium [5] show that the accumulation of Si^{2+} ions near in layers at the electrodes can cause a significant concentration-dependent polarization. The dependence of the polarization on the experimental conditions is included to first approximation in the formula:

$$\eta_{\kappa,a} = \mp \frac{RT}{2F} \ln\left(1 + \frac{\delta}{2FD_2N_2^0}i\right)$$
(3)

Here the sign $\mp$ is for the cathode and anode polarization, respectively, i is the current density, δ is the diffusion layer, N_0^2 /376 is the initial concentration of Si^{2+} ions in the electrolyte, and D_2 is their diffusion coefficient. If N_2^0 is small, then:

$$\mp \eta_{\kappa,a} = \frac{RT}{2F} \ln \frac{\delta}{2FD_2N_2^0}i.$$
(4)

From this it follows that the polarization can be rather large in the absence of a limiting current. Thus the earlier basic argument [1] against a concentration-dependent polarization is not valid in this case.

The assumption of the formation of bivalent silicon at the electrodes allows other properties of the observed polarization to be explained qualitatively. Thus, the protracted growth of the polarization when the current is turned on and the slow decay, which allows the polarization to be "frozen", can be accounted for by the small value of the diffusion coefficient of Si^{2+} ions in the viscous electrolyte. Furthermore, the decrease in the growth of the polarization as the current is increased, that is, the

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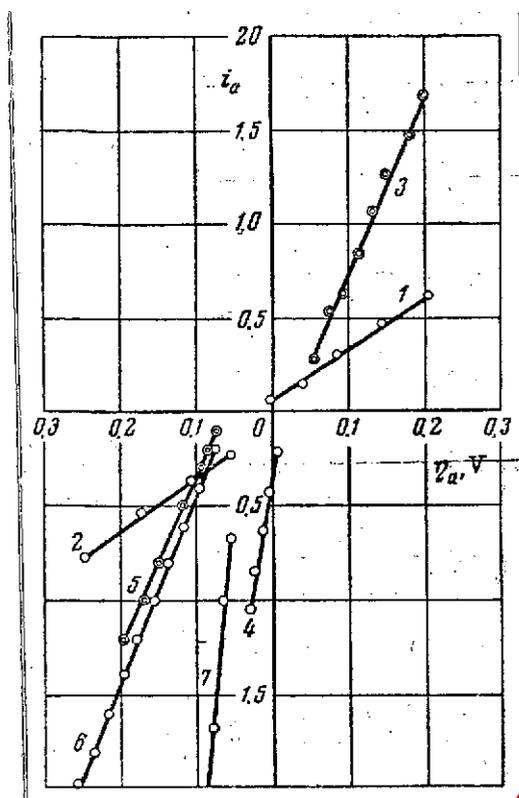curvature in the "line" relating η and i, follows directly from the logarithmic character of Equation (4).

Figure 2. Polarization curves for ferrosilicate electrodes (22.5% Si) and an electrolyte consisting of 30% SiO_2, 50% CaO, 10% Al_2O_3 and 10% MgO. Annode curve 1 and cathode curve 2 at 1440° C; annode curve 3 and cathode curves 5 and 6 at 1500° C; cathode curves 4 and 7 at 1540 and 1600° C, respectively
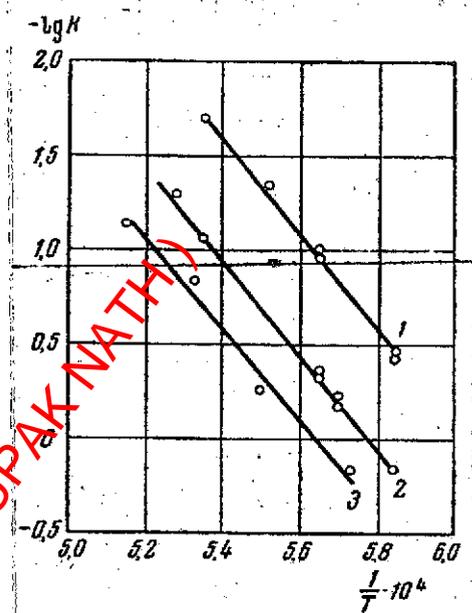
Figure 3. Dependence of the slope (k) of the linear portions of the polarization curves on temperature. Lines 1 and 2 are for ferrosilicon electrodes and electrolytes containing 30% SiO_2 and 50% SiO_2; Line 3 is for a ferrophosphorus cathode and an electrolyte containing 43% SiO_2.

Moreover, the slope of the curve

$$\frac{d\eta}{di} = \frac{RT}{2F}\frac{1}{i} = \frac{RT}{2F}\frac{\delta}{2FD_2N_2^0}e^{\pm\eta\frac{2F}{RT}} \qquad (5)$$

for a fixed value of η becomes smaller as the diffusion coefficient and the temperature increase, according to Equation (5). In other

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words, the curvature in the "lines" should occur sooner at higher temperatures, which is confirmed experimentally.

The equality of the coefficients k_K and k_a and their exponential dependence on temperature follow from Equation (5). Setting

$$D_2 = D_2^0 e^{-E_2/RT}, \quad | \tag{6}$$

we find that

$$k_K = k_a = \left| \frac{d\eta}{di} \right| = \frac{RT}{2F} \frac{\delta}{2FD_2^0 N_2^0} e^{\frac{E_2 \pm \eta 2F}{RT}}, \quad | \tag{7}$$

from which

$$k_K = k_a = k^0 T e^{(E_2 \pm \eta 2F)/RT} \quad | \tag{8}$$

Here the activation energy is

$$E = E_2 \pm \eta 2F \quad |$$

and does not depend on the electrolyte material for a given value of η in agreement with experiment.

Finally, the absence of polarization in electrolytes with a small silica content (less than 20% SiO_2) is probably caused by the fact that bivalent silica cannot exist in melts with that composition.

However, explaining the occurrence of polarization by the accumulation of Si^{2+} ions at the electrodes leads to difficulties. Thus, for example, a ferrophosphorus anode contains almost no silicon. Thus the electrochemical formation of Si^{2+} ions from the reaction (2) is impossible here (in the required volume). It is true that this contradiction could be explained by assuming that phosphorus (and iron) ions transport from the anode into the fused silicate. Their initial concentration in the electrolyte is small, as with the Si^{2+} ions. Thus in this case the

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concentrational polarization is determined by an expression analogous to Equation (4), that is, it will have the same properties as for the formation of Si^{2+} ions.

The small value of N_0^2 and its indeterminateness should strongly affect the slope of the polarization curves, and sometimes give them random values. This was not observed. However, the irregular variation of the coefficients k_K and k_a with silica concentration in the melt could be noted in favor of this effect. These coefficients were higher for 40% SiO_2 than for 30% and 50% SiO_2.

It is difficult to reconcile the linear variation of η and i over wide intervals of their values with Equation (4). The actual slopes of these lines experimentally increase with temperature for both a given polarization and for a fixed current. Conversely, it follows from Equation (5) that the linear proportionality between $\ln k$ and $1/T$ is possible only for a given polarization. For a fixed current, the polarization should increase linearly with temperature. This was not observed, however.

In conclusion, we note that the hypothesis of a retarded orientation and deformation of complex ions also runs into difficulties. For example, it should be expected that saturation would be reached at higher values of the polarization as the tem-   /378 perature increased. However, experiment showed that the distortion of the straight lines started at smaller values of η as the temperature was increased.

In summary, the hypothesis of accumulation of bivalent silicon ions near the electrode can explain just as many facts as the hypothesis of retarded orientation and deformation of complex ions.