

**CORROSION PROTECTION
OF MATERIALS IN ANY MEDIA
AND CONDITIONS**

Formation, Retention, and Discharge of Products of Atmospheric Corrosion of Metals. 4. Model: Corrosion–Discharge of Products

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Abstract—An empirical mathematical model $K = K_0 + km_{10s}$ (relating atmospheric corrosion to the weight loss of its products) for incubation + transient and steady-state stages of the process, is considered. To develop the model, we used the results of long-term (from 3 month to 1–17 years) field tests of metals according to the Russian, International ISOCORRAG, and Russia–Vietnam–Cuba programs. The K_0 and k factors in the model were determined according to the corrosion of Cr3, copper, brass, zinc, aluminum, D16 alloy, and AMu alloy in the zones of cold, moderate, subtropical, and tropical climates. The model quantitatively relates the corrosion losses of a metal to those of the products discharged to the environment. It may be useful when it is necessary to estimating the amount of detrimental metals, e.g., unprotected copper and zinc dispersed to the environment, but there is no data on the weight of products that had been retained by the metal in the air.

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INTRODUCTION

Earlier [1, 2], we considered the variation in the total weight of test specimens of carbon steel, zinc, copper, magnesium, aluminum, its alloys of D16 and AMu types, and brass, as well as the weight variation of the atmospheric corrosion products retained by the specimens, as a function of corrosion losses in various climatic zones and at various test duration. A mathematical model of the overall weight of corrosion products was proposed. It enabled one to estimate also (some input model parameters being known) the discharge of the corrosion products into environment [1, 2]. In [3], the $m/K = f(K)$ dependence of the retained products weight m per unit weight of the total corrosion losses weight K was analyzed for the above metals in cold, moderate, and tropical climates.

Estimates of discharge the dispersion of environmentally dangerous copper and zinc products according to the model [1, 2] show that it depends on both the climatic characteristics of a region and the pollution level of its atmosphere with corrosive agents promoting corrosion of the metals.

Here, we continue recent studies [1–3] and propose a model that quantitatively relates the total corrosion losses of metals to the weight of products dispersed to the environment. Practically, in the absence of quantitative data on the weight of corrosion products retained

on the metals, this model can be useful when estimating the weight of the products dispersed.

RESULTS AND DISCUSSION

The Effect of the Products Retained on Inhibiting the Corrosion

The expected corrosion losses over the long periods of time can be determined by an equation:

$$M_\tau = M_1 \tau^n, \quad (1)$$

where M_τ is the corrosion weight loss of a metal (g/m^2) over the time τ (years) from starting the exposure, M_1 is the corrosion weight loss over a year (g/m^2), and n is the factor characterising the effect of products on the corrosion rate [4, 5]. M_1 is the most important parameter. The annual corrosion losses due to the entire cyclic variation in the weather and concentrations of corrosive air components immediately reflect the overall characteristic of the atmospheric corrosivity to a metals, yearly repeated on the average. For this very reason (for unalloyed carbon steel, copper, zinc, or aluminum), according to the ISO 9223:92 international standard, the level of atmospheric corrosivity is determined in any region. The Standard involves five classes of the atmospheric corrosivity starting from “insignificant S1” to “very strong S5” [6].

Based on our previous and available literature results of the corrosion tests of metals at 104 stations (in Australia, Brasilia, Vietnam, Nigeria, Panama, Baltic Sea region, Russia, the USA, Czechia, Sweden, and Japan) for the first-year M_1 and the subsequent years of exposure M_r , using Eq. (1), we obtained actual magnitudes of exponent n and proposed mathematical equations to calculate the input parameter n in eq. (1) [5]:

carbon steel, zinc, copper:

$$n = 1 - ab^{-1/M_1}, \quad (2)$$

aluminum:

$$n = ab^{-1/M_1}, \quad (3)$$

Here a and b are constants individual for rural, industrial, and marine atmospheres. These coefficients were determined by solving a system of many equations of type (1) for any metal by its observed corrosion in the corresponding areas.

Depending on the atmospheric corrosivity, especially in seaside, coefficient n varies in a rather wide range: from 0.4 to 0.6, for unalloyed carbon steel; from 0.3 to 0.8, for aluminum; from 0.7 to 1.0, for zinc; and from 0.3 to 0.7, for copper. The higher the atmospheric corrosivity, the larger the n . The corrosivity of atmosphere in Eqs. (2) and (3) is indirectly taken into account by parameter M_1 . The predictive estimation of corrosion losses with Eqs. (1) and (2, 3) yields an error within $\pm 20\%$, which is quite allowable for engineering goals [5].

Model Eqs. (1–3) involve no evident parameters characterizing the protective properties of products retained by metals. Predictive mathematical models relating the corrosion weight loss of a metal to the protective properties of corrosion products are still unknown. Can there be any practical prediction mathematical model that relates varying the corrosion losses to one or several characteristic parameters of corrosion products, such as, their composition, structure, porosity, etc.? The question is not positively answerable to day.

The composition and structure of corrosion products retained on the metal surface and transformed with time, have been studied rather thoroughly [7–11]. It was shown that, in different areas with insignificantly differing atmospheric corrosivity the corrosion products on metal are almost identical, have similar structures, compositions, and percent ratios between the amounts of their chemical components. For instance, a layer of patina on copper, which was exposed at 39 test stations in Europe, contained predominantly cuprite Cu_2O , brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$, and posnikite $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$. Their average percent contents in patina were 57, 34, and 8%, respectively [12]. On unalloyed carbon steel, rust contains predominantly oxide monohydrate (lepidocrocite $\gamma\text{-FeOOH}$ and goethite $\alpha\text{-FeOOH}$, whose percent content varies with aging

and depends on the atmospheric pollution with sulphur dioxide and chlorides) and small amounts of Fe_2O_3 and Fe_3O_4 oxides [7–11]. On zinc, the corrosion products are commonly hydroxide–salt, for example, $\text{ZnCO}_3 \times 3\text{Zn}(\text{OH})_2$, $\text{Zn}_5\text{Cl}_2(\text{OH})_8$, or $\text{Zn}_4\text{SO}_4(\text{OH})_6$ [7].

The protective properties of dry corrosion products, which form on the metals: Be, Mg, Ca, Al, Nb, Ta, Ti, Cr, Mo, W, Mn, Fe, Ni, Co, Zn, Cd, Cu, Sn, Pb, Sb, Bi, Pd, Pt, Ag, Au, and In, upon mechanically trimming their surface and exposing to the air, wet H_2S , or 10% $\text{K}_2\text{Cr}_2\text{O}_7$ solution, were judged from varying their electric resistance and breakdown potential [13]. For some metals (zinc and carbon steel covered with corrosion products formed as a result of four-year exposure in the air and in louver huts in rural areas), the products were studied by voltammetric and ohmic-capacitance methods [7, 14].

The presence of native oxide or artificial chromate film on the metals considerably enhanced the resistivity of almost all metals. By contrast, after exposure in wet H_2S , the ohmic resistance of surface layer of corrosion products on the metals abruptly decreased (for Nb, Ta, Cr, Mo, W, Fe, Ni, Co, Zn, Cd, Cu, Sn, Pb, Sb, and Bi, by one–three orders of magnitude compared to the native oxide film). Unlike this, the resistivity and breakdown potential increased to 30–400 V and 3–4 V for Ca and Ti, respectively [13]. A linear dependence between the thickness of corrosion products and the breakdown potential was observed. The effect of the product layer thickness depends on the type of metal: on steel, the products 30–40 μm thick (the thickness was calculated by the weight of products retained on the metal) with a breakdown potential of 200–300 V exhibited lower corrosion resistance than the products to 5 μm thick on zinc with a breakdown potential no higher than 10–40 V [7].

The characters of the corrosion inhibition on steel and zinc surfaces also differ. On steel, in the initial period, the corrosion process is controlled by the destruction rate of the original oxide film. The rate is considerably inhibited with a significant increase in the product layer thickness, that is, to a decrease in the area of active zones on the metal surface. On zinc, a significant decrease in the corrosion rate in the initial period is caused by the formation of thin insulating hydroxide layer. In the presence of the layer, atmospheric corrosion proceeds only in its pores almost from the very beginning. The presence of thin insulating layer is verified by an increase in the cathodic and anodic polarizability, a significant decrease in the capacitance, and an increase in the resistance of zinc specimen in the 0.1 N NaCl solution. The steady-state potential of zinc is invariant for a long time and independent of the amount of products. This indicates that zinc products are not involved in the electrochemical process [7, 14].

Thus, the corrosion process is determined by the properties of oxide layer immediately adjacent to the metal and its breakdown caused by the medium corro-

sivity. Visible and, especially, readily removable phase layers of products, probably, only in special cases (carbon steel) can inhibit the atmosphere corrosion. One should also take into account the indirect role of the products. They considerably absorb moisture and corrosive impurities from the air and, hence, can either increase the electrolyte corrosivity to the metal or mechanically hamper the access for the impurities to the metal surface. Of course, both the effects can manifest themselves simultaneously depending on the morphology of the product layer and factors acting at this very moment: chlorides and SO_2 , adsorption or phase layer of moisture, the intensity of rains, temperature, etc.

Consequently, the above facts make it important to analyze the dependence of metal weight loss on the parameters of retained corrosion products. Taking into account that, in [13], the thickness of dry products was estimated by the total weight of products formed, we use two parameters: the weight of retained products m , g/m^2 and dimensionless parameter m/K characterizing their weight per unit weight of corroded metal.

Let us compare the kinetics of variations in parameters m and K for the plane and spiral specimens in an unpolluted atmosphere (Oimyakon) and marine atmosphere (Vladivostok and Murmansk). At two latter stations, both the duration of wet state of metal surface and the atmosphere salinity (estimated in accordance with the ISO 9223 Standard [6]) are similar; however, the stations differ in the concentrations of sulfur dioxide in the air and the intensity of rains that simultaneously affect the removal of both soluble corrosive components and corrosion products from the metal.

The highest retention of products (300–400 g/m^2) on steel plates is observed in Vladivostok only in the first year of exposure. In Murmansk, the retention to 600 g/m^2 is observed for 4–5 years, Fig. 1. Then, m varies jumpwise within narrow limits. On steel wire spirals, m is higher. It is to 500 g/m^2 in Vladivostok in the first and subsequent years, but in Murmansk, the amount of retained products increases progressively and reaches 1200 g/m^2 by 8 years. In a unpolluted atmosphere of Oimyakon, m is also higher on the spirals than on the plates.

In Murmansk and Vladivostok, the corrosion losses K in the first years are comparable; however, after a four-year exposure, in Murmansk they are lower on the plates and much lower on spirals than in Vladivostok, Fig. 2. That is, at significantly larger weight m of retained products, in Murmansk, the corrosion is retarded stronger, than in Vladivostok, where m is smaller. At the same time, at each station, corrosion of spirals is considerably stronger than that of plates, though the weight of retained products is larger on spirals, and they formed under similar conditions of exposure of plates and spirals.

On nonferrous metals, the weight of retained products significantly increases in the first two, less com-

monly, 4–5 years. Then, the weight increase is retarded (zinc in Murmansk), significantly retarded (aluminum and its alloys in Murmansk, zinc in Vladivostok, aluminum in Oimyakon), or becomes almost zero (copper, aluminum and its alloys in Vladivostok, copper in Murmansk, zinc and copper in Oimyakon). The corrosion losses of nonferrous metals (plates and wire spirals) in Murmansk exceed those in Vladivostok, and, at both stations, they are larger on spirals. With an increase in the amount of products, after 1–2 years, in Murmansk, the corrosion rate retards for copper, remains almost invariant for zinc, slightly increases for aluminum, and significantly retards for alloys. In Vladivostok, this trend is stronger, especially on aluminum and its alloys, though the weight of retained products on metals is considerably smaller. The general tendency to the increase in the weight of retained products with an increase in the corrosion losses is observed also in the case of two-year exposure of metals in humid tropics in Cuba and Vietnam, in humid subtropics in Batumi, and in the moderate climate in Zvenigorod.

This comparison indicates that, in any individually considered climatic area, both on the plates and spirals, the growing with time amount of corrosion products to more or less retards the corrosion. However, when comparing the corrosion of metals in different areas, the opposite conclusion can also be made: the weight of retained products grows with an increase in the corrosion intensity. The conclusions seem to contradict; however, each of them is quite probable. In the first case, the products impede the access to the anodic zones on the metal for the corrosive components. The second case is probably characteristic of porous thickening layers of products collecting concentrated electrolyte for a long time thus providing the continuity of anodic and cathodic reactions in the metal–products interface wetted with the electrolyte.

To explain the seeming contradiction, let us consider the variation in the m/K parameter with time, Fig. 3. In a short period of exposure ($\tau \rightarrow 0$), the weight of retained products is comparable with the weight of the products formed, m_f , i.e. the discharge of the products is virtually absent ($m \rightarrow m_f$), and $m/K \rightarrow A$. Here, A is a constant determined by the nature of prevailing chemical compounds, that is, the corrosion products. The weight of the products formed can be expressed as follows:

$$m_f = AK, \quad (4)$$

An analysis of eq. (4) showed that, for the identified chemical compounds in the corrosion products on Al, Mg, Fe, Zn, and Cu, the range of A variation is not too wide [1, 2].

Parameter m/K significantly decreases with time in Vladivostok and only slightly does in Oimyakon. Consequently, in Vladivostok, the products are lost especially from the spiral specimens, quicker and are replaced by new products. Thus, although their total

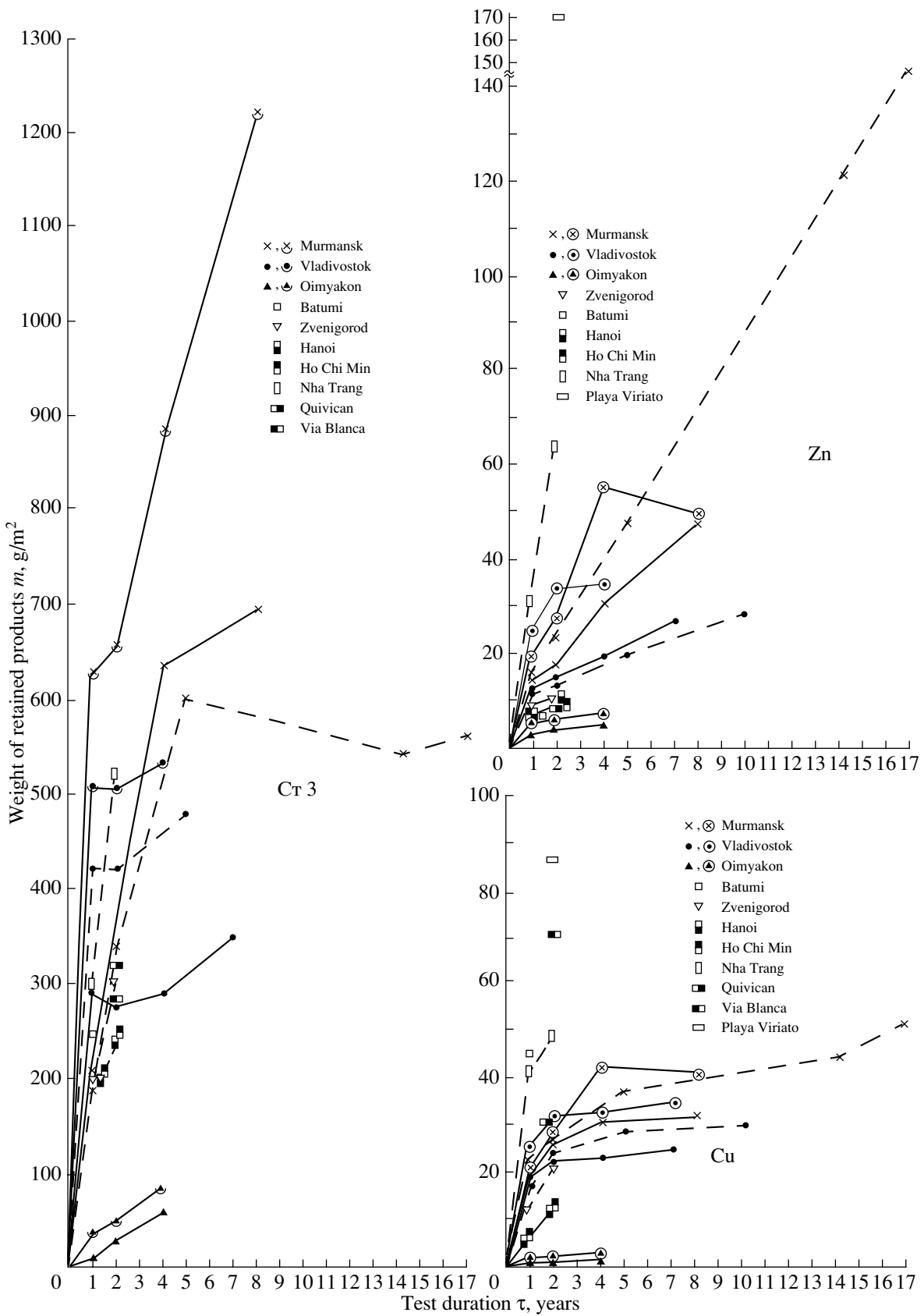


Fig. 1.

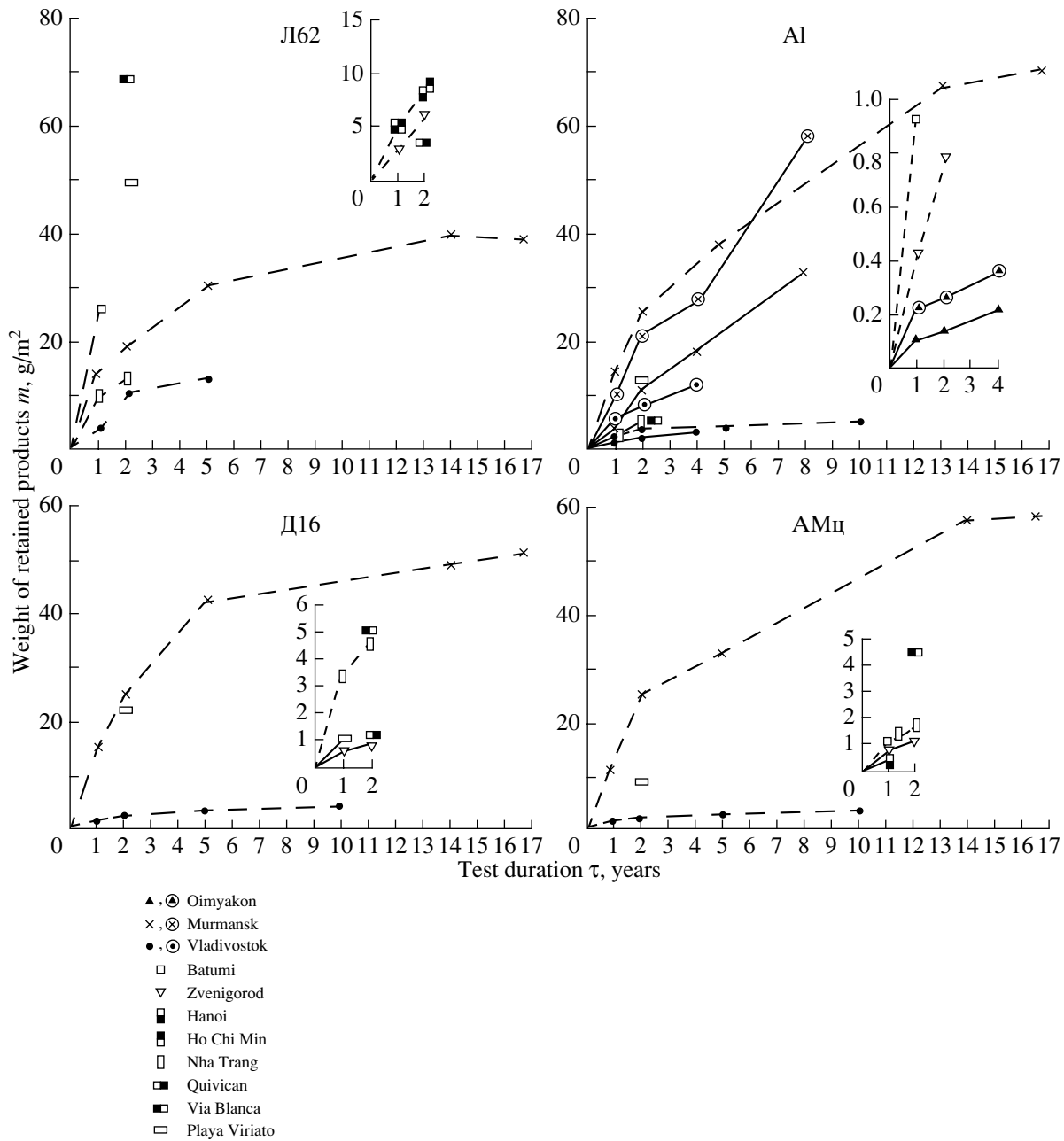


Fig. 1. Kinetics of the growth of weight of retained products on carbon steel, zinc, copper, aluminum, and its alloys. Experimental data obtained according to the Russian Program of full-scale tests (1984) and International Program ISOCORRAG (1987) are shown with solid lines. The data of the Russian-Vietnam-Cuba Program are shown dashed. Symbols correspond to the test stations: ●, ⊙, ⊙ Vladivostok, ×, ⊗, ⊗ Murmansk, ▲, ▲, ▲ Oimyakon, □, □ Batumi, ▽ Zvenigorod; ■ Hanoi; ■ Ho Chi Min, □ Nha Trang, ■ Quivican, ■ Via Blanca, □ Playa Viriato. Symbols ●, ⊗, ▲ and ⊙, ⊗, ▲ correspond to the spiral specimens of wire 2 and 3 mm in diameter, respectively; the rest symbols correspond to the plates.

weight increases, they are in fact relatively “young” and do not reliably protect the metal against destruction. This opinion is real, if the K and m/K values are compared in equal periods of time. For example, in Vladivostok, corrosion of steel plates in 4 years is by 1.02 and 20.5 times higher and corrosion of wire spirals is by 2.6 and 45.3 times higher than in Murmansk and Oimyakon, respectively. However, the weight of retained

products per unit corrosion m/K in the same time period is considerably smaller in Vladivostok than in Murmansk (by 2.3 and 4.3 times on plates and spirals, respectively), and even smaller if compared with Oimyakon: by 4.0 and 7.2 times for the same specimens. In Vladivostok, K of spirals is higher than K of plates by 3.4 times; however, parameter m/K is lower by 1.9 times for spirals than for plates.

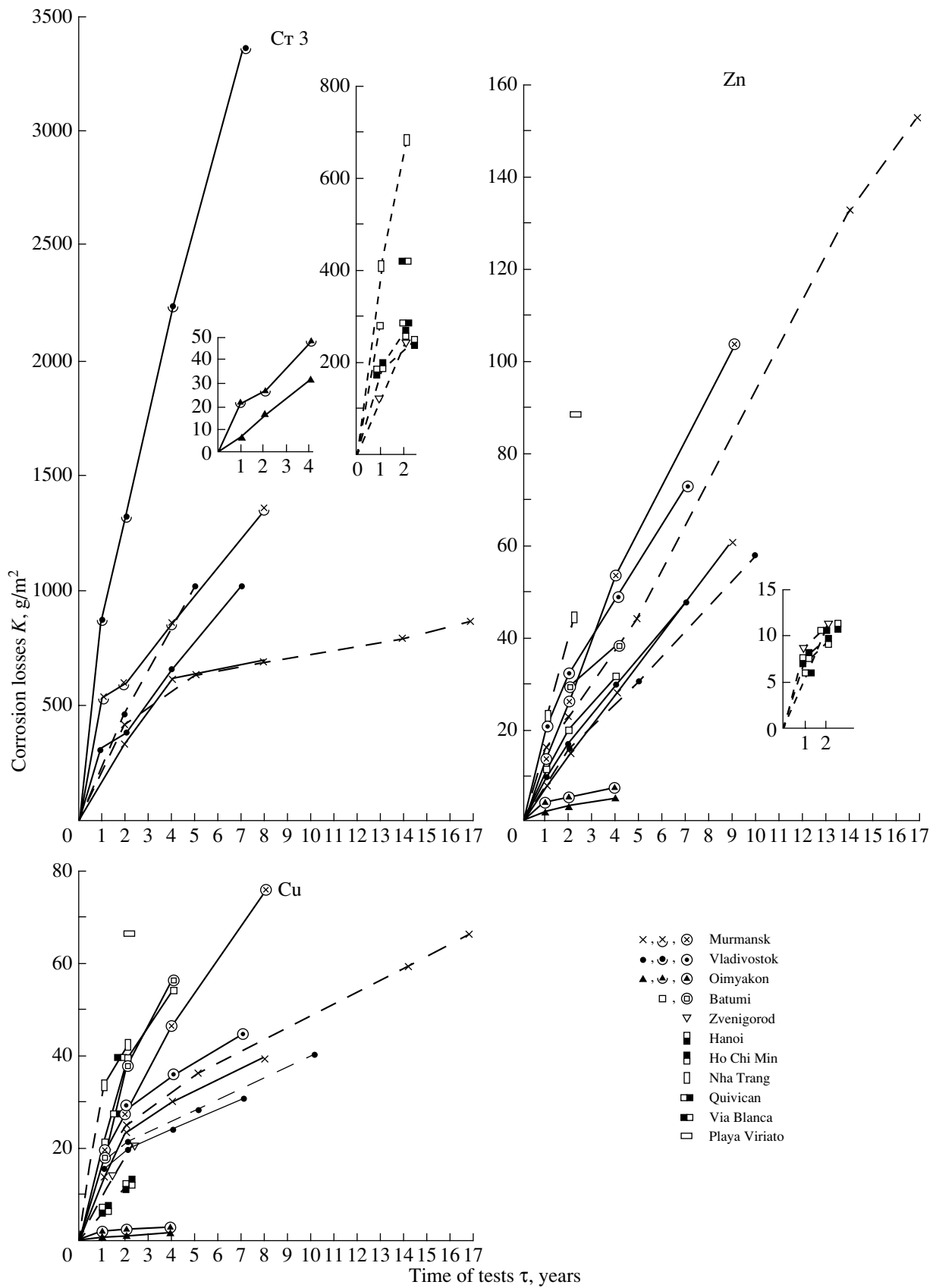


Fig. 2. Kinetics of corrosion weight losses of metals with time. For symbols see caption to Fig. 1.

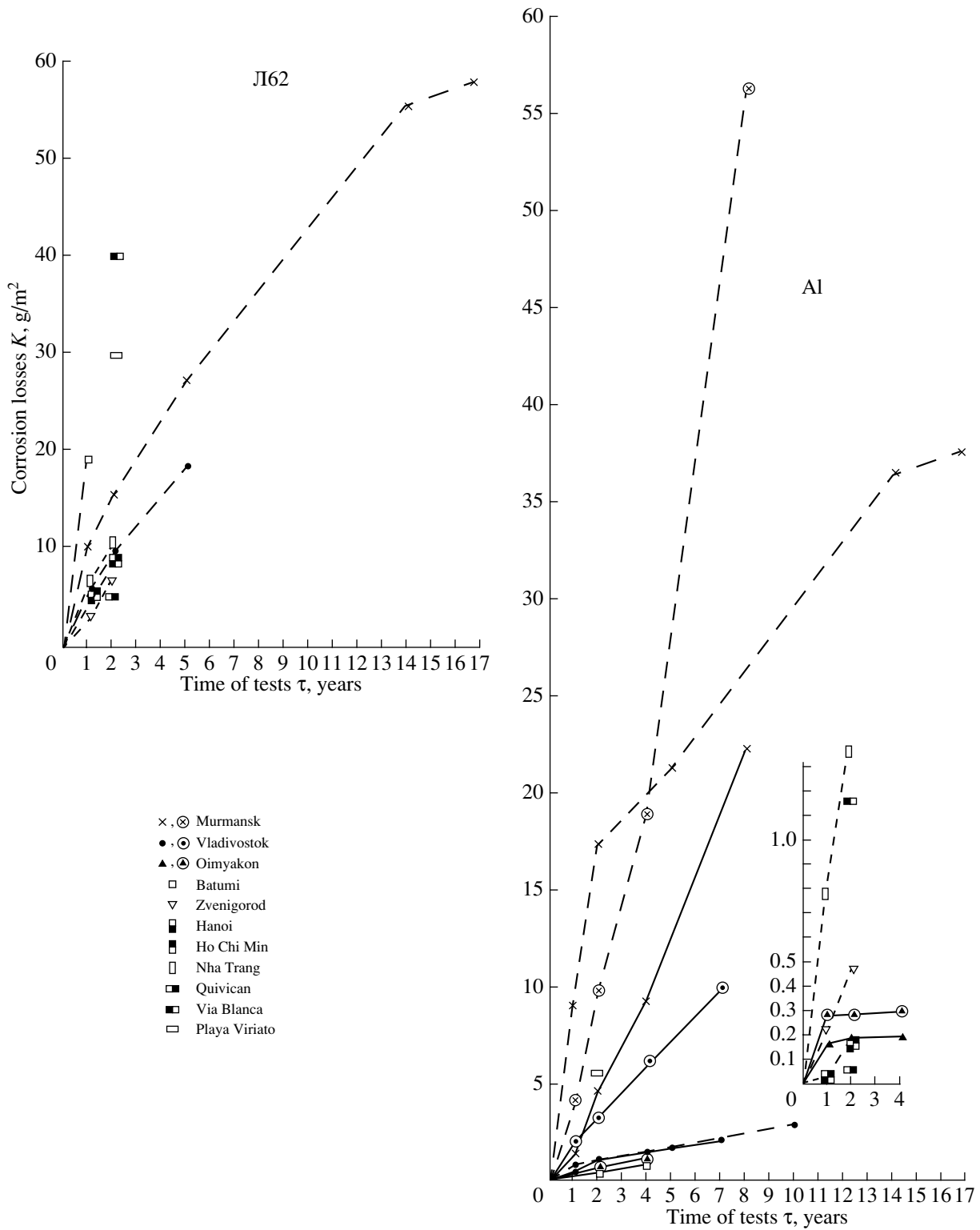


Fig. 2. (Contd.)

Weak retardation of corrosion by “young” products of carbon steel exposed for 2 years in the tropics in Via Blanca (industrial–marine atmosphere) and Nha Trang (marine atmosphere), where corrosion of steel is

severe, is also the evidence of relatively low m/K parameter (0.65 and 0.75, respectively). However, at other stations in Russia, Cuba, and Vietnam, where the corrosivity of atmosphere is lower, substitution of

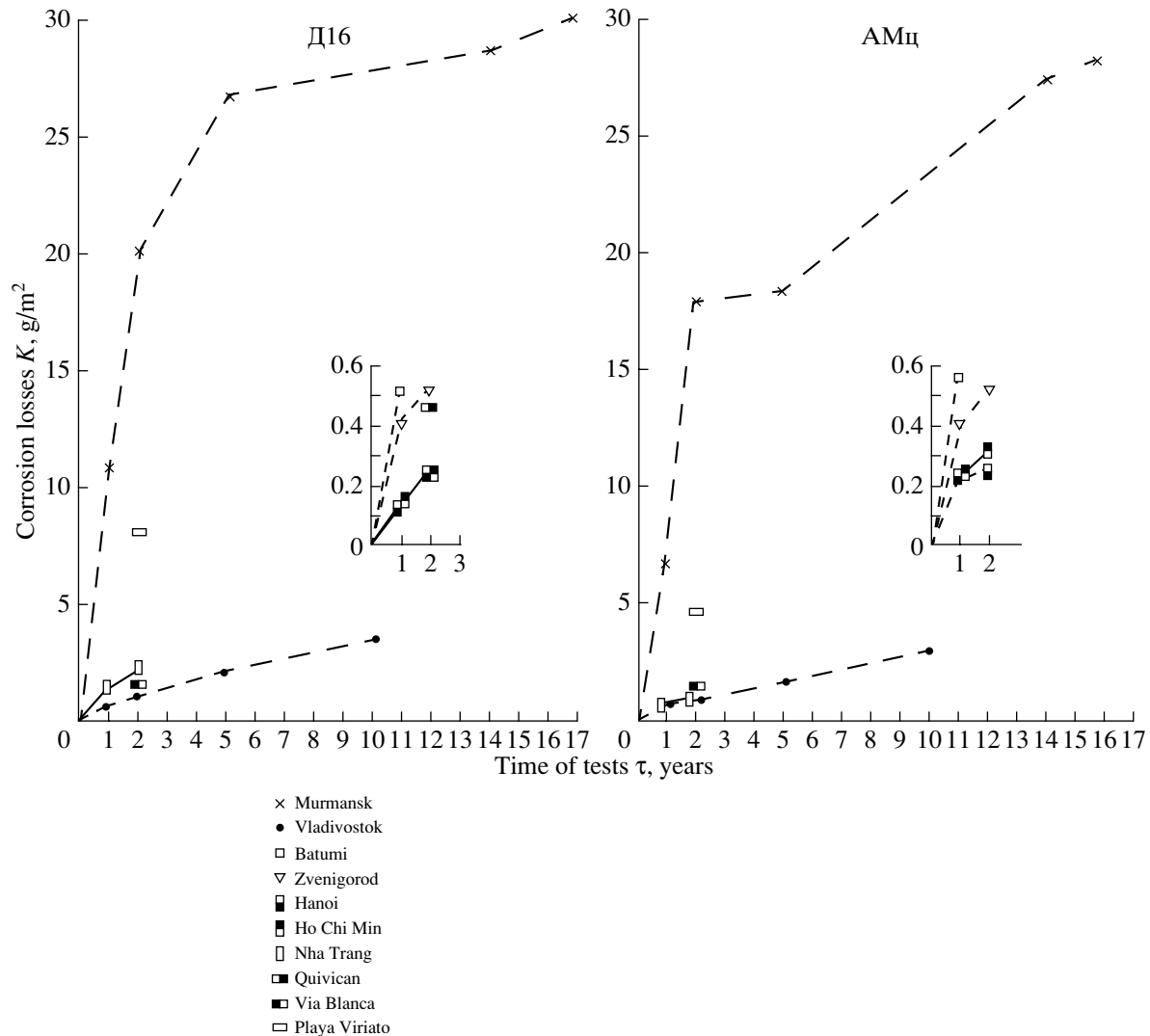


Fig. 2. (Contd.)

“young” products for old ones proceeds not so quickly and they continue to noticeably retard corrosion judging from relatively high parameter $m/K = 0.9\text{--}1.2$, Fig. 3.

For nonferrous metals (zinc and copper), the m/K values decrease with time and remain rather close. However, the m/K parameter of these metals is lower in Vladivostok than in Murmansk and for spirals than for plates. In relatively unpolluted atmospheres in Vietnam, Cuba, and Russia, according to the data of two-year tests, m/K falls in ranges of 0.7 to 0.9 and of 1.0 to 1.2 for zinc and copper, respectively, whereas, in the corrosive atmospheres of Nha Trang, Via Blanca, and Playa Viriato, the m/K variation range is wider: from 1.3 to 1.9 and 1.2 to 1.5. A similar trend is observed for brass. Hence, it may be concluded that corrosion of zinc, copper, and brass is determined by the corrosivity of electrolyte formed at the metal and the ability of retained products to accumulate salt and gas promoters of corrosion.

For aluminum and its alloys, m/K varies within wide ranges and ambiguously with time, which makes their analysis difficult. Even comparing the variation kinetics of three parameters: K , m , and m/K (Figs. 1–3), it is difficult to judge the variation of m/K parameter with time. Aluminum and its alloys are not resistant against chloride ions, which cause pitting. The retention of Cl^- on the metal depends on the frequency and intensity of rains [15]. In Murmansk, with a rain intensity of 0.1–0.2 mm/h, chlorides precipitated on the metal surface, are rinsed weakly. They are retained by salt deposits and corrosion products, especially, in the pits. In Vladivostok, despite the similar average salinity of atmosphere, marine salts are washed off by more intense rains (1–2 mm/h); as a result, corrosion of aluminum and alloys is by an order of magnitude lower than in Murmansk. Even in Playa Viriato, where both atmosphere salinity (to 400 mg Cl^-/m^2 day passes to the underlying surface from air) and the intensity of rains

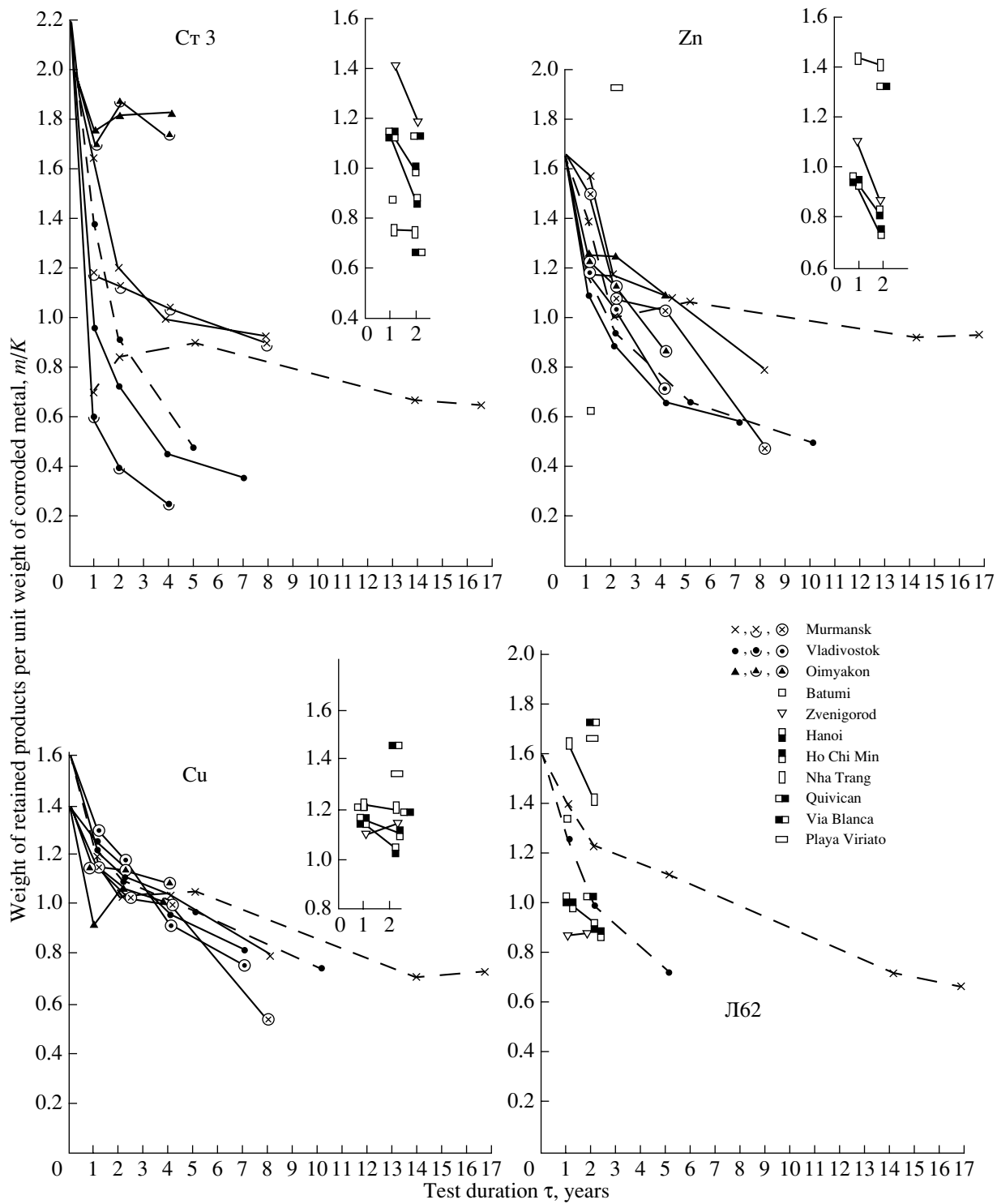


Fig. 3. Kinetics of variation in the weight of products, which are retained on the specimen, per unit weight of corroded metal. For symbols see caption to Fig. 1.

(2–9 mm/h) are very high; total corrosion losses of aluminum in 2 years were only 5.4 g/m² and the weight of retained products was 12 g/m². This is 3 and 2 times lower, respectively, than in Murmansk for the same exposure time.

Thus, the experimental results show that in the case of damping corrosion, the destruction of metal is considerably retarded with oxide, hydroxide, and salt corrosion products (on zinc, copper, aluminum and its alloys, and carbon steel) in the first–second, less com-

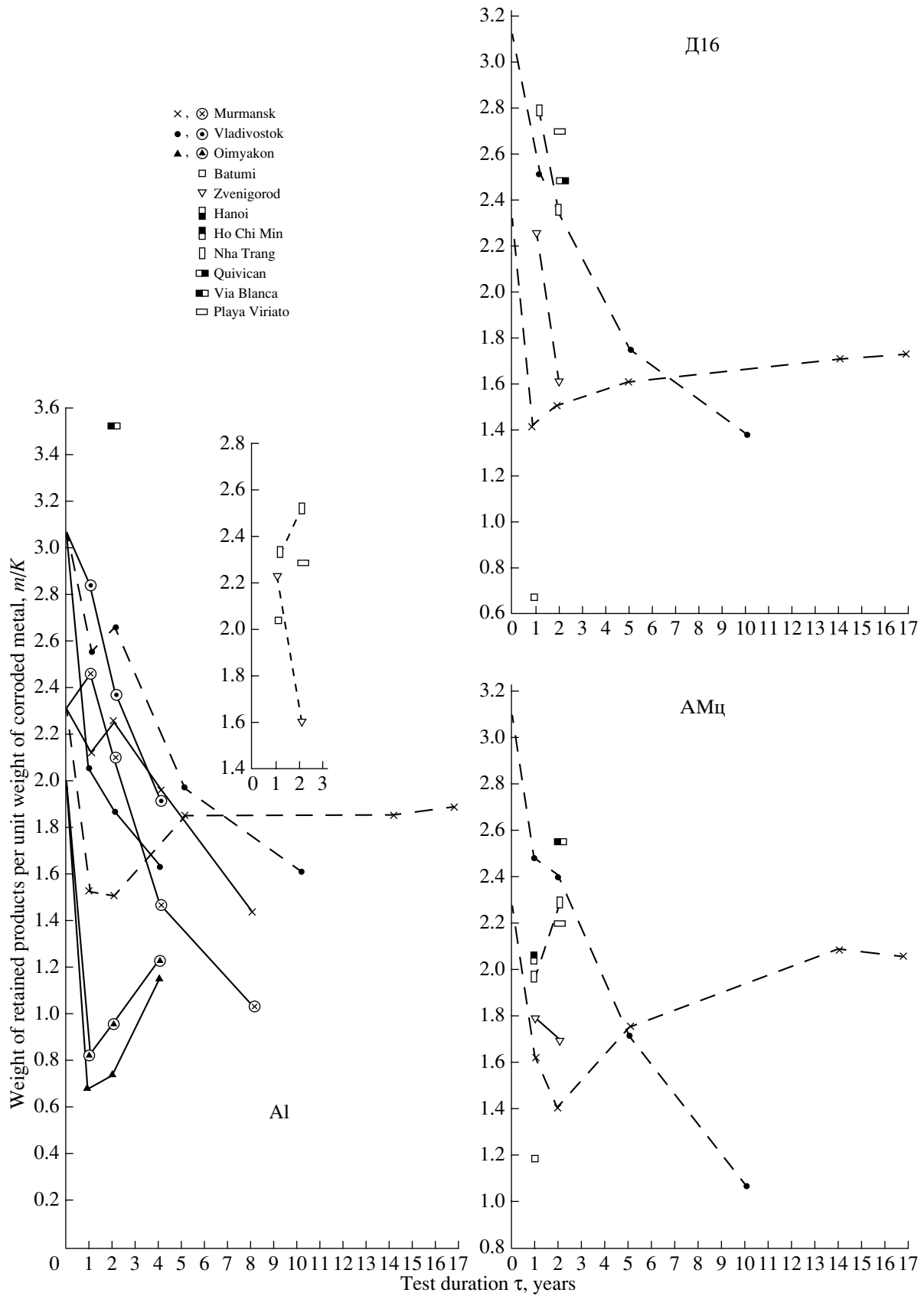


Fig. 3. (Contd.)

monly, in the fourth–fifth year of exposure to the open atmosphere. When a certain steady-state thickness is reached, the products retard the diffusion flow of the environmental corrosive components to the metal surface with different degrees of effectiveness. The surface existence of the products is not everlasting. The products are subjected to the dissolution with neutral and, especially acidic rains, weathering, crumbling down, and cracking; however, the weight of products retained by metal is stabilized with time. Their partial loss is continuously compensated by the formation of fresh portions of products. The protective properties of products are not directly related to their weight. They are determined by their chemical and physical nature that depends on the aerochemical and climatic parameters of the environment jointly affecting the metal and its corrosion products.

Simulation of Interrelation between the Corrosion Losses K and the Weight of the Lost Products m_{lost}

The idea of substantiating the model, which quantitatively relates the corrosion losses to a single parameter characterizing the corrosion products, in particular, m or m/K , is very attractive, but scarcely practicable.

Earlier [3], we analyzed actual changes in m and m/K for various metals, when they corroded in the open atmosphere in the areas with cold, moderate, and tropical climates. For experimental mathematical model of $m/K = f(K)$ type, individual equations were obtained that enable one to calculate the necessary coefficients (for steel, zinc, copper, and aluminum) involved in the function $m/K = f(K)$. It seems that, using the plots of $m = f(K)$ and $m/K = f(K)$ types constructed by the experimental data, we could obtain the curves of $K = f(m)$ and $K = f(m/K)$ dependences like those given in Fig. 4 by simply rotating the axes by 90° and reflecting the plots.

It is seen from Fig. 4a that the corrosion losses K steeply increase with an increase in m . At a certain limiting weight of retained products m , parameter $K \rightarrow \infty$, which is absurd from practical point of view. The plot on Fig. 4b also does not clarify the essence of virtual chemical or physical correlation between K and the variation in m/K . Obviously, an attempt to develop a practical mathematical model of the dependence of total metal corrosion weight on the parameter m or m/K is hopeless. It is much more real to use, (as such a parameter), the weight of the products (m_{lost}) were lost from the metal surface throughout the course of corrosion. The weight of the lost products, as well as the weight of the metal corrosion losses, is determined by the intensity of weather factors and corrosive impurities in the air, continuously or periodical increases with time.

Figure 5 gives the variations in m , m_f , and m_{lost} of the plates and spirals exposed concurrently in Murmansk and Vladivostok. The weights of retained products m (experimental results), formed products m_f (calculated

by equation $m_f = AK$ (where constant A is 2.1 and 2.0 for Vladivostok and Murmansk, respectively [1, 2]), and lost products m_{lost} (calculated by equation $m_{\text{lost}} = m_f - m$) correspond to real corrosion losses K . In the plots, circles B_i and B'_i for plane and spiral specimens correspond to the experimental values m ; circles A_i and A'_i correspond to the calculated values m_f ; sections of dashed lines $A_i B_i$, for plates, and $A'_i B'_i$, for spirals, correspond to the calculated values m_{lost} . Subscript $i = 1, 2, 4, 7, \text{ and } 8$ indicates the exposure time (years) of the specimens. Comparing K , m_{lost} , and m for equal exposure times at different or individual test stations, one can see that the weight of lost products is the predominant parameter in the corrosion process.

In Vladivostok, m of carbon steel varies in time insignificantly but the fraction of lost products m_{lost} significantly increases and, by 4–7 years, reaches 79–83% and 89–92% m_f on plates and spirals, respectively. Corrosion losses of spirals and plates over equal periods of exposure for spirals, K is commonly larger by a factor of 2.8–3.3; the discharge of products from spirals appears to be by 3.7–3.9 times larger, Table 1.

In Murmansk, due to the climatic conditions (low intensity of rains, the absence of dry periods in winter season, which can affect the cracking and falling the products off), the weight of retained products increases in the course of corrosion but slowly; by 8 years, a fraction of lost products on steel plates and spirals is about 54% of the products formed. Compared with Murmansk, in Vladivostok, the corrosion losses for 4–7 (or 8) years, become by 10–50% larger for plates and by 2.5–2.6 times larger for spirals, whereas m_{lost} increases by 70 and 140% and 4.4–5.0 times, respectively, Table 2.

Tables 1 and 2 list similar data for nonferrous metals. For these metals, the loss of products is predominantly associated with their dissolution and removal with rain water and, to a lesser extent, with their falling off and weathering. With respect to m_f , a fraction of the lost zinc and copper products reaches 40% and more by 7–8 years. Therewith, it is larger on spirals than on plates by 10 to 60% and 1.6–4.7 times, and the corrosion losses also appear to be larger by 1.3–4.5 and 1.2–3 times in Vladivostok and Murmansk, respectively.

The higher corrosion rate of wire spirals is commonly explained by identifying it with the intenser corrosion of upper side of a plate facing the sky, assuming that the corrosion conditions for them (the chloride precipitation rate from air, moistening the surface with rain, heating by solar radiation, etc.) differ only little. However, this isn't always true for all metals. For instance, by the results of tests performed in the USSR [16] and Vietnam [17], the total corrosion losses of the upper side of Cr3 plate were smaller than the losses recorded on its lower side facing ground; however, in the cases of zinc and copper plates, the reverse situation

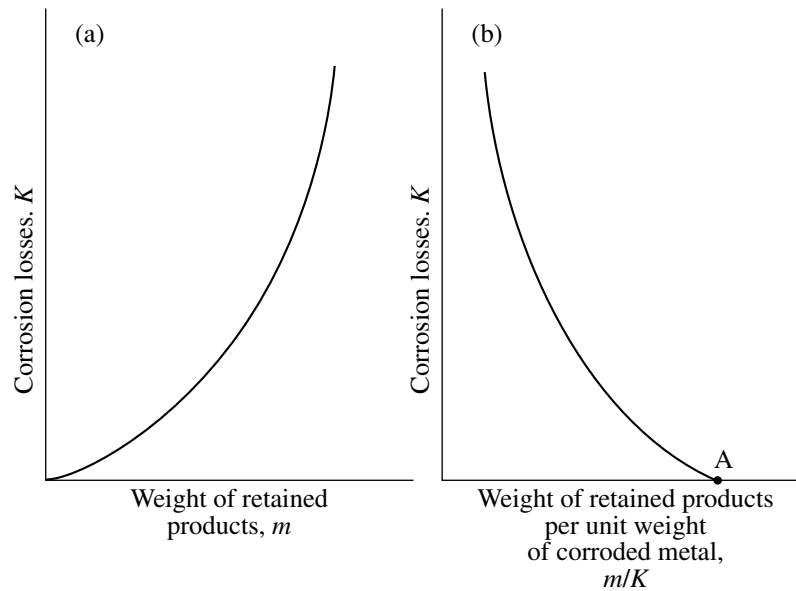


Fig. 4. Plots illustrating in general form the correlation between the corrosion losses and (a) the total weight of retained products and (b) their weight per unit weight of corroded metal.

was observed, Fig. 6. Direct rain moistens the entire surface of wire spiral, thus promoting its corrosion; for a plate, in this case, the lower side more frequently remains dry. The intensity of spiral corrosion cannot be related uniquely to the effect of washing off its products by rain water. Discrete areas of the surface of a wire spiral have different inclinations. With an increase in the inclination angle to the horizon of steel, zinc, and copper plates from 20° to 45° , their corrosion decreases [18]. At a significant inclination, water wets the entire surface and quickly flows off removing the accumulated salts. This is supported by a considerable decrease in the corrosion losses of plate specimens with an increase in its inclination angle in the highly saline atmosphere of Playa Viriato, in the industrial-marine atmosphere of Via Blanca, and in the rural atmosphere of Guira de Melena, Table 3 [18].

Thus, as a whole, in different test regions, the corrosion losses are determined by both the corrosivity of atmosphere (the corrosivity of electrolyte formed directly on the metal) and the discharge of the products. In each climatic zone, the discharge of the products increases with an increase in the corrosion rate.

Thus, we can suppose that, in long-term atmospheric tests, parameter m_{lost} , which increases with time and comprises a considerable fraction of the total weight of the corrosion products formed, is quite appropriate when characterizing the corrosion process. It depends on the composition of the corrosion products formed, aerochemical parameters of the atmosphere, and, especially, the climatic parameters promoting mechanical failure, dissolution, as well as weathering, of the corrosion products. The corrosion process proceeding under its products and decelerating with time,

should not be totally ignored. It continues with a certain rate under the dynamic conditions of the partial loss of the products and their regeneration.

Taking into account the known coefficient A , which is responsible for the composition of products formed on the metals studied, we calculated the weight m_{lost} :

$$m_{\text{lost}} = AK - m, \quad (5)$$

and the dependence of K on m_{lost} (Fig. 7). In general case, the growth of the products layer on the metal is classified with incubation, transient, and steady-state periods. The first two periods include destructing the initial oxide film and forming the layer of intermediate and final products. On common carbon steel, they take months in a humid corrosive atmosphere and three–four years in an unpolluted atmosphere. When the metal becomes entirely coated with the products and is seemingly in the equilibrium with environment, the steady-state period begins: relatively constant corrosion rate, which is determined by the barrier properties of the products, is reached [19].

Judging from the experimental points in Fig. 7, the K correlates with the products discharge as follows: relatively steep initial growth of K with an increase in m_{lost} gives way to a monotonic retardation and then, the variation rate of K remains almost constant and linearly depends on m_{lost} . Taking into account three aforementioned periods of the metal oxidation, the initial growth and subsequent retardation of K evidently correspond to the incubation and transient stages; when the variation rate of K ceases to change, the steady-state stage is reached.

It is not always possible to simulate exactly the entire process. Therefore, taking into account that in the

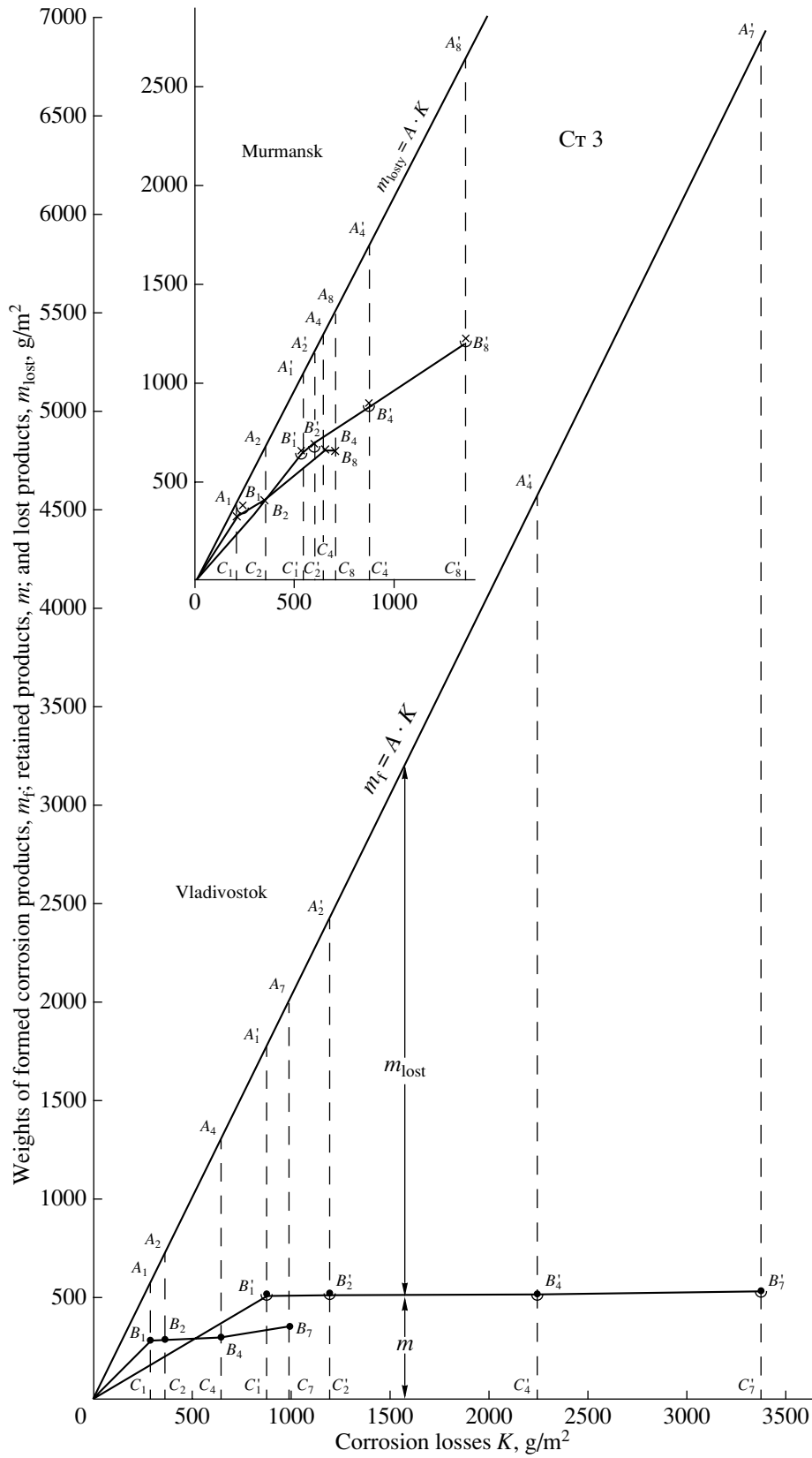


Fig. 5. Variations in the weights of formed products m_r (ordinates of segments $A_i C_i$ and $A'_i C'_i$), retained products m (ordinates of $B_i C_i$ and $B'_i C'_i$), and lost products m_{lost} (ordinates of $A_i B_i$ and $A'_i B'_i$) in the course of corrosion of plates and wire spiral specimens of carbon steel, zinc, and copper. Subscript i indicates the duration of tests, years.

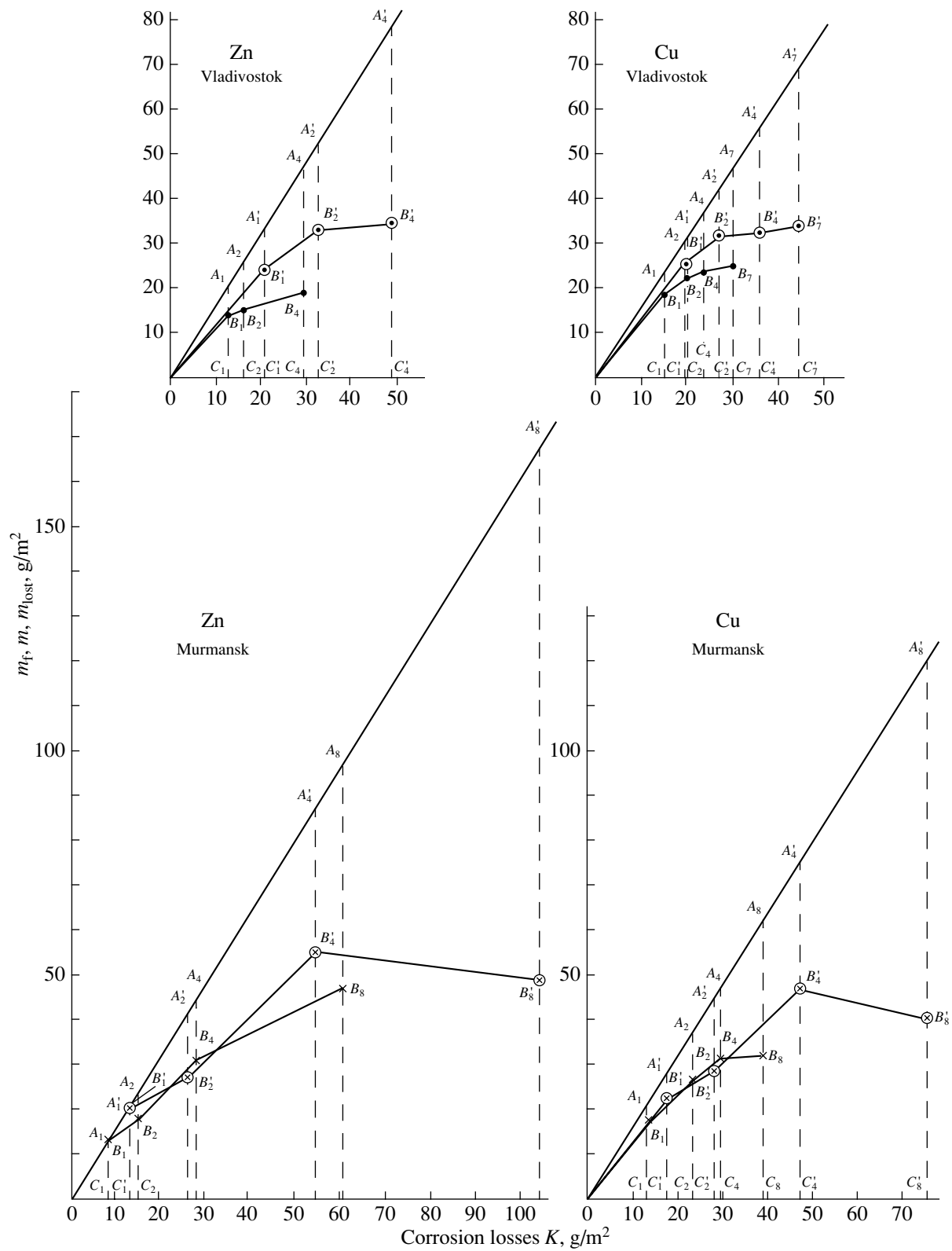


Fig. 5. (Contd.)

Table 1. Time variation of the ratios of corrosion parameters for plate and wire spiral specimens (m_{lost} is the weight of lost products, m_f is the weight of formed products, and K is the corrosion)

Years	$(m_{lost, plate}/m_{f, plate})/(m_{lost, spiral}/m_{f, spiral}), \%$				K_{spiral}/K_{plate}				$m_{lost, spiral}/m_{lost, plate}$			
	Fe	Zn	Cu	Al	Fe	Zn	Cu	Al	Fe	Zn	Cu	Al
Vladivostok												
1	55/70	34/28	23/19	33/8	2.8	1.6	1.3	3.9	3.7	1.3	1.1	0.9
2	66/82	46/37	28/26	39/23	3.5	2.0	1.4	3.1	4.3	1.6	1.2	1.8
4	79/89	60/57	40/42	47/23	3.4	1.7	1.5	4.0	3.9	1.6	1.6	1.0
7	83/92	67/–	48/51	–	3.3	–	1.5	4.5	–	–	1.6	–
Murmansk												
1	18/42	5/9	2/17	8/–	2.6	1.6	1.3	3.0	6.1	3.1	2.0	–
2	40/44	29/36	20/27	2/9	1.7	1.7	1.2	2.1	1.8	2.1	1.6	10.2
4	48/49	35/38	26/27	16/36	1.4	1.9	1.6	1.6	1.4	2.0	1.6	4.7
8	54/55	52/71	42/61	37/55	1.9	1.7	2.0	1.8	2.0	2.4	2.8	3.7

Table 2. Relative estimation of corrosion losses and the weight of lost products in Vladivostok (K_V and $m_{lost,V}$) and Murmansk (K_M and $m_{lost,M}$); pl are the plates, sp are the spirals; 1–8 is the time of tests, years

Parameter, the type of specimen		Steel 3				Zinc				Copper				Aluminum			
		1	2	4	7–8	1	2	4	7–8	1	2	4	7–8	1	2	4	7–8
K_V/K_M	pl	1.49	1.09	1.02	1.45	1.50	1.10	1.04	0.79	1.06	0.83	0.80	0.77	0.31	0.23	0.17	0.10
	sp	1.62	2.24	2.60	2.50	1.56	1.24	0.91	0.70	1.06	0.96	0.76	0.58	0.47	0.34	0.32	0.20
$m_{lost,V}/m_{lost,M}$	pl	4.81	1.86	1.75	2.36	10.9	1.73	1.79	0.98	2.41	1.39	1.41	1.02	1.67	6.74	0.68	–
	sp	2.93	4.34	4.96	–	4.67	1.27	1.38	–	1.32	1.06	1.37	0.56	–	1.21	0.45	–

first two stages, K and m_{lost} increase slowly, whereas the third stage is in a first approximation linear, the common model function relating K to m_{lost} for two first, as well as the third, stages can be represented in a linear form:

$$K = K_0 + km_{lost}, \tag{6}$$

Here, K_0 and k are the calculated coefficients listed in Table 4. Obviously, in the first two stages, coefficient K_0 characterizes the corrosion losses (g/m^2) associated with the destruction or transformation of initial oxide film on the metal, which are not accompanied by a considerable discharge of corrosion products. Coefficient k represents the corrosion losses to a moments when the metal loses $1 g/m^2$ of the products. Probably, at the transient stage, when K and m_{lost} are not yet very large, coefficient k characterizes more likely (in a mathematical aspect) an average variation in the slope of the linear function (6) in a range of small variations in parameters K and m_{lost} rather than the corrosivity of the atmosphere. However, at the steady corrosion stage, k can be considered as a characteristic of the atmosphere corrosivity. In a group of some, atmospheres, the most corrosive is one that exhibits the highest K (as well as k) at one and the same discharge of the products. In other words, the

more corrosive the atmosphere the higher the k , and the quicker the products are discharged (m_{lost}), the higher are the corrosion losses.

In long-term corrosion tests, the steady-state stage (that is, the linear dependence) becomes pronounced, when K and m_{lost} increase to a certain level. Extrapolation of straight line (eq. 6) to the ordinate axis yields a new value K_0 corresponding (to a first approximation)

Table 3. One-year corrosion weight loss (g/m^2) of plates inclined to the horizon by various angles

Station, atmosphere	Metal	20°	30°	45°
Playa Viriato, marine	Steel 3	3354	2750	2180
	Aluminum	9.0	8.2	6.7
	Copper	63.2	60.9	55.2
Via Blanca, industrial–marine	Steel 3	494	420	370
	Aluminum	1.3	1.1	1.0
	Copper	35.2	34.1	30.4
Guira de Melena, rural	Steel 3	243	236	220
	Aluminum	0.4	0.35	0.1
	Copper	13.6	12.7	11.2

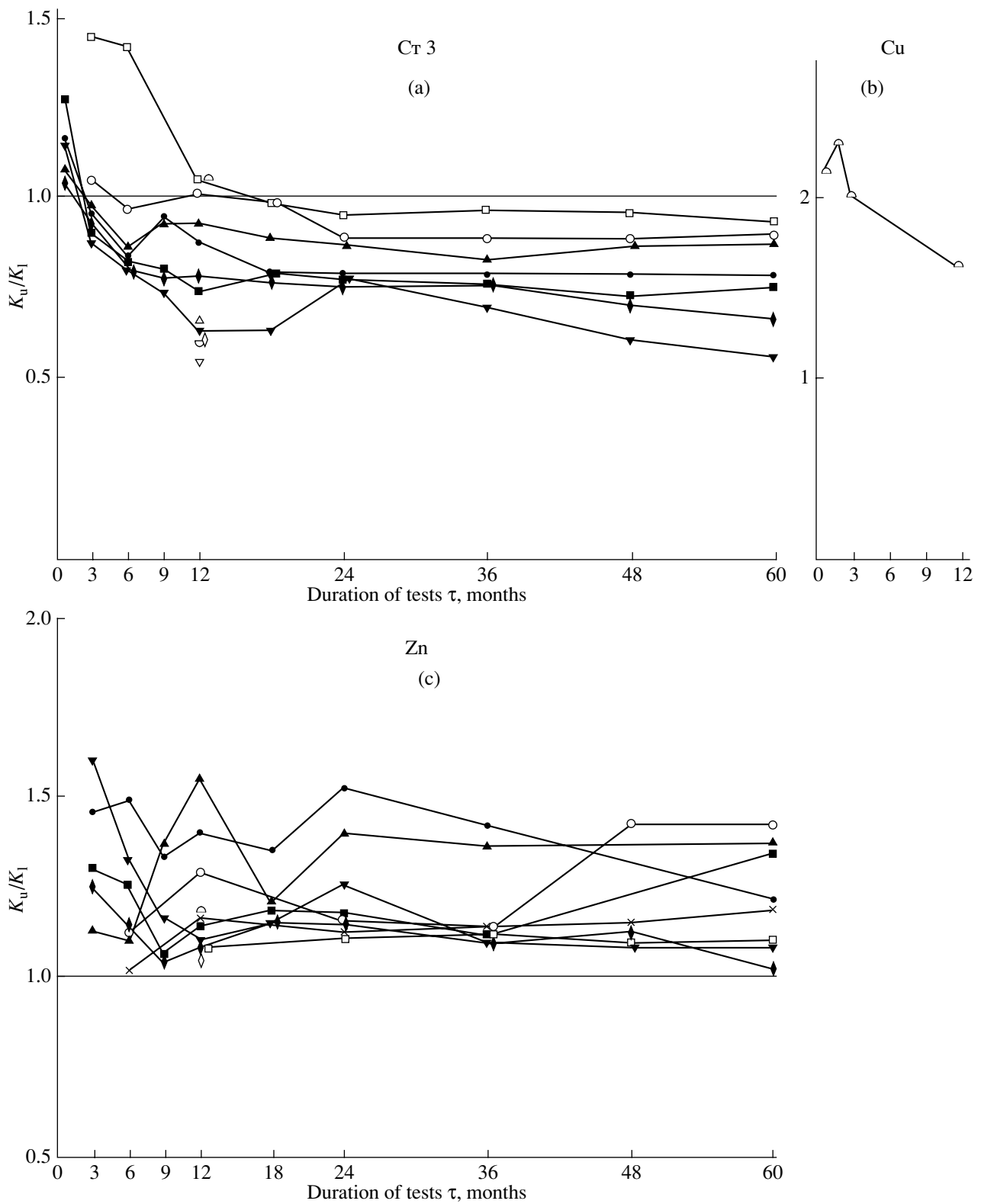


Fig. 6. The ratio of corrosion losses on the upper side of plate to those on the lower side: (a) carbon steel, (b) copper, and (c) zinc. Symbols correspond to the following test stations: ● Hanoi, ▲ Vinh Fu, ▼ Haiphong, ■ Vinh, ◆ Hon Zau, × Da Lat, ○ Ho Chi Min, □ Kien Zhang, ◇ Moscow, ▽ Zvenigorod, △ Murmansk, ◊ Batumi, and △ Vladivostok.

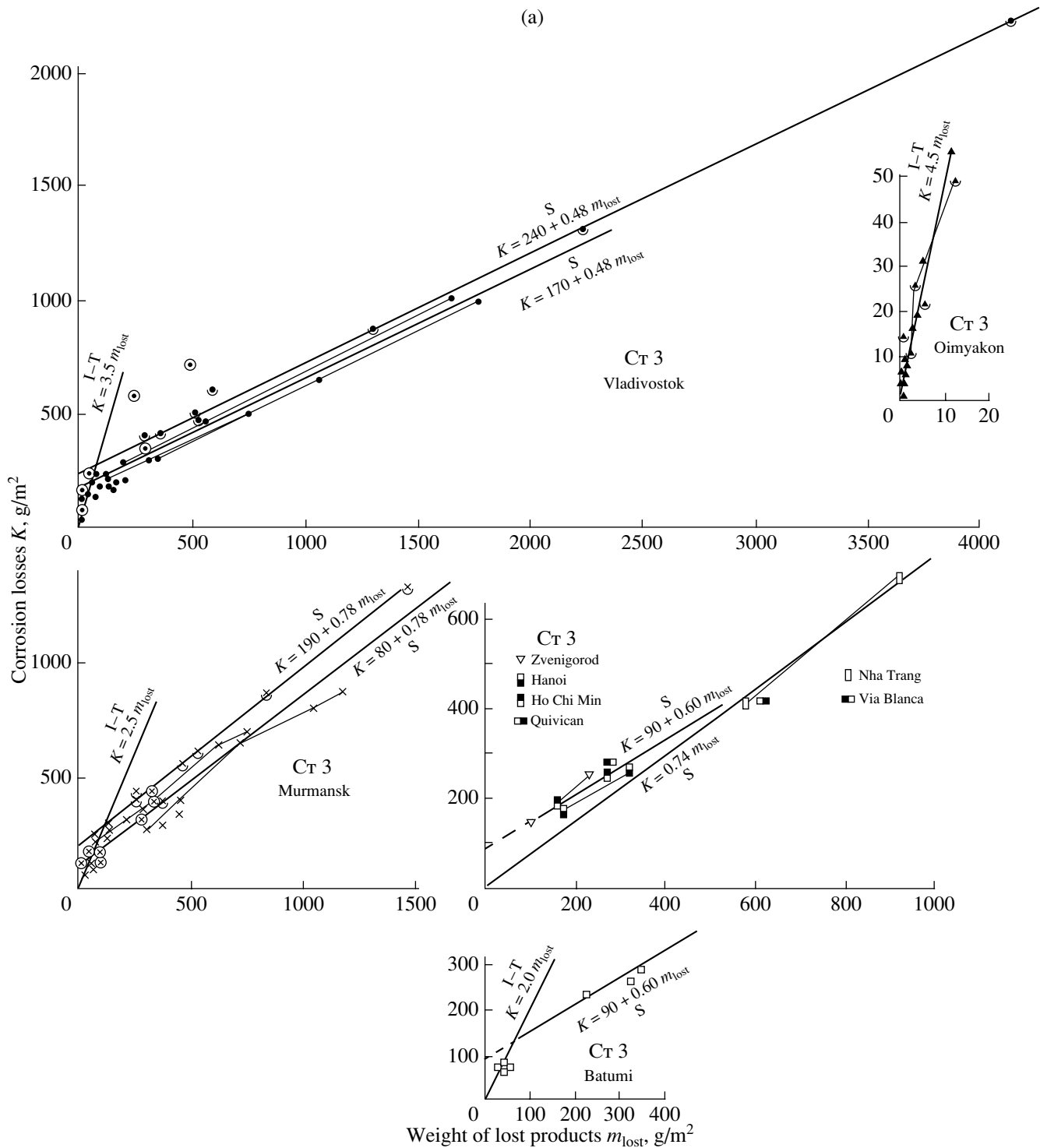


Fig. 7. Dependence of the corrosion of plates and wire spirals on the discharge of the products of atmospheric corrosion to the environment: (7a) Cr 3, Zn, Cu, Л62, Al, Д16. For symbols see Fig. 1. Letters I-T and S at the plots mean the incubation–transient and steady-state stages of corrosion process.

to the corrosion losses (somewhat underestimated by extrapolation) for the first two stages (ignoring the discharge of products).

Carbon Steel, Fig. 7a. For steel in the incubation stage, K_0 is approximately zero. By the results of short

(three-month) tests of steel plates and spirals in Murmansk and Vladivostok, we can consider that the transient stage was finished when the corrosion losses reached approximately 200 g/m², whereas the lost part, to 100 g/m². In Batumi, it finished at smaller K and m_{lost} .

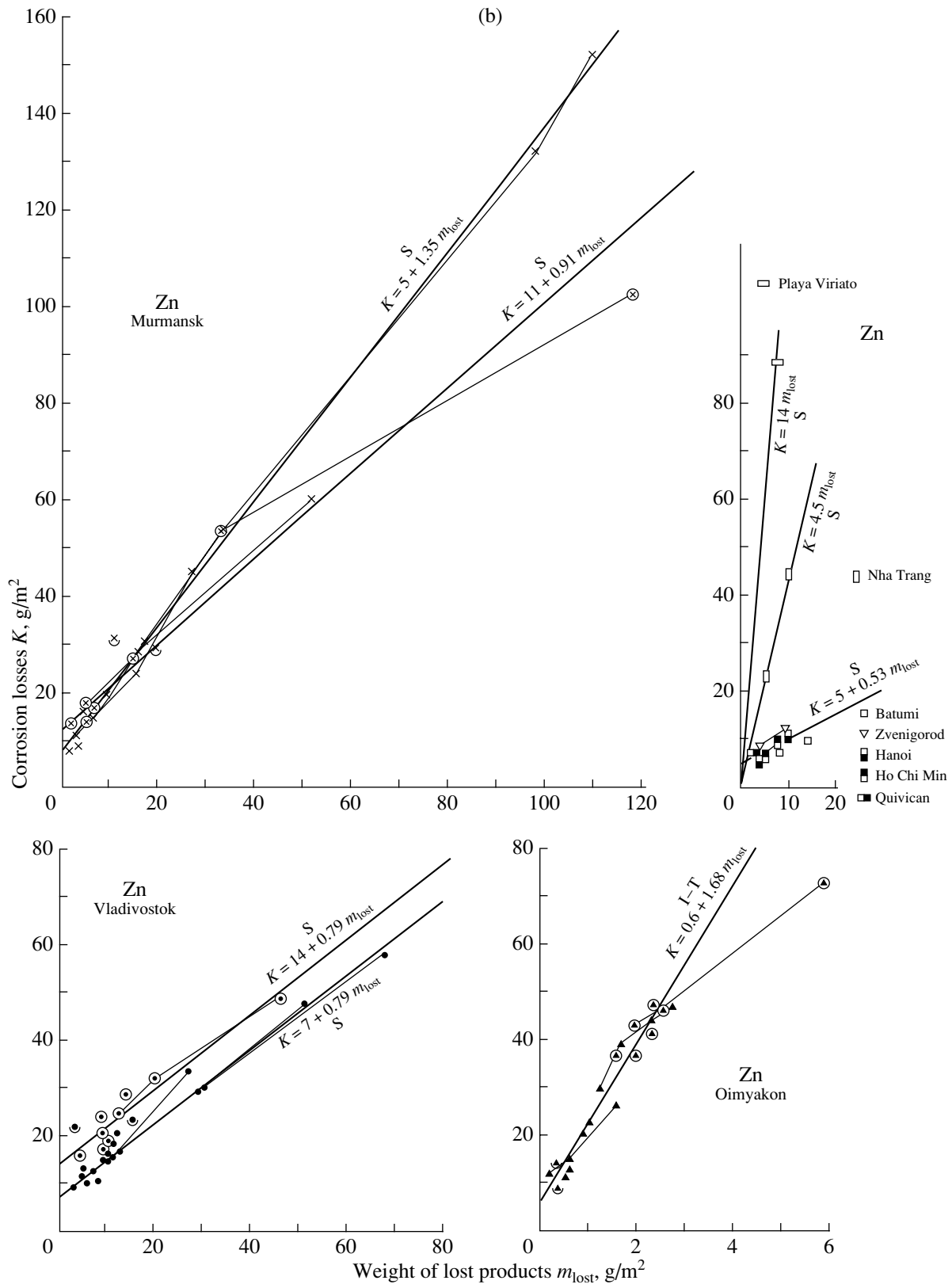


Fig. 7. (Contd.)

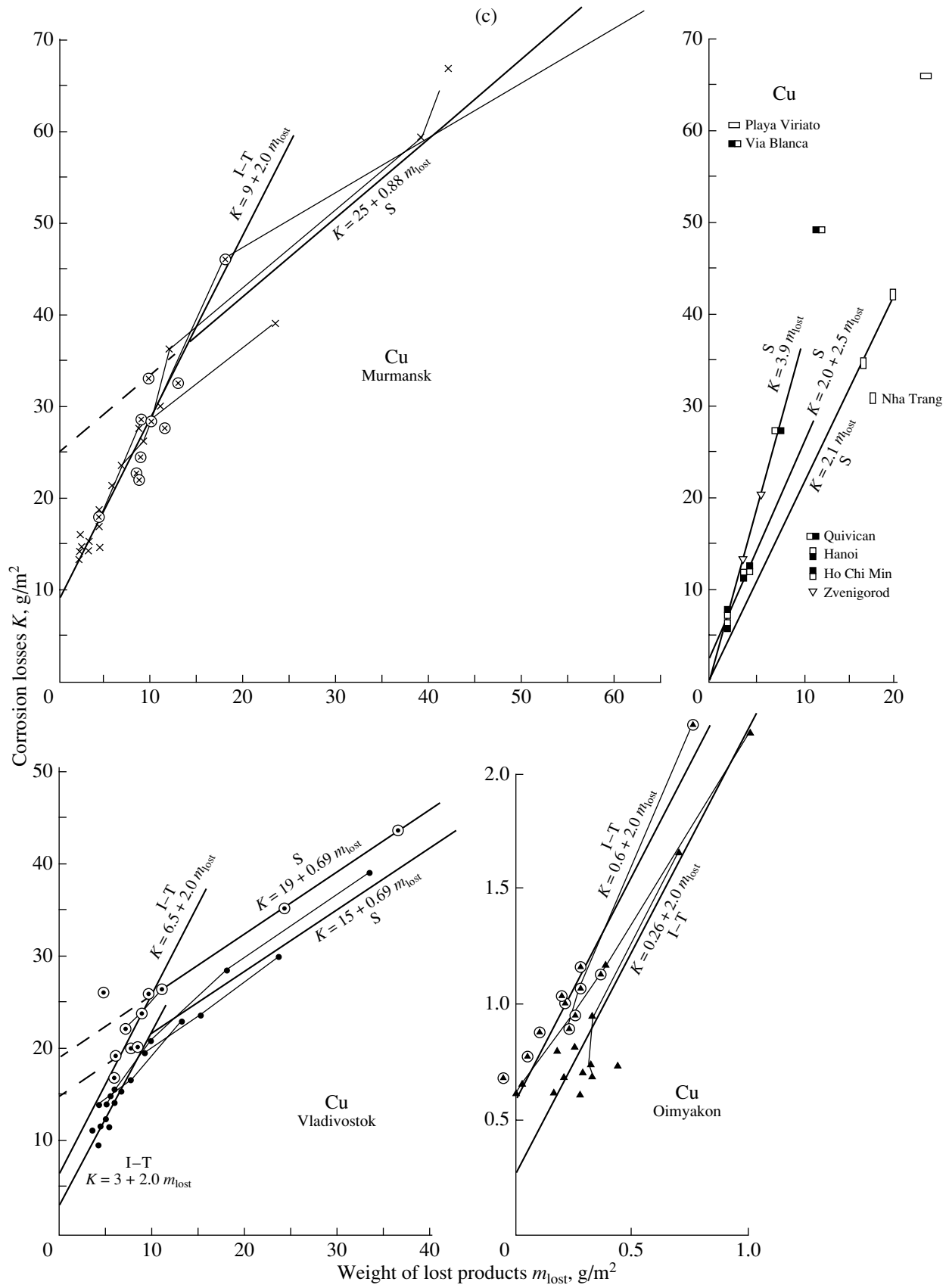


Fig. 7. (Contd.)

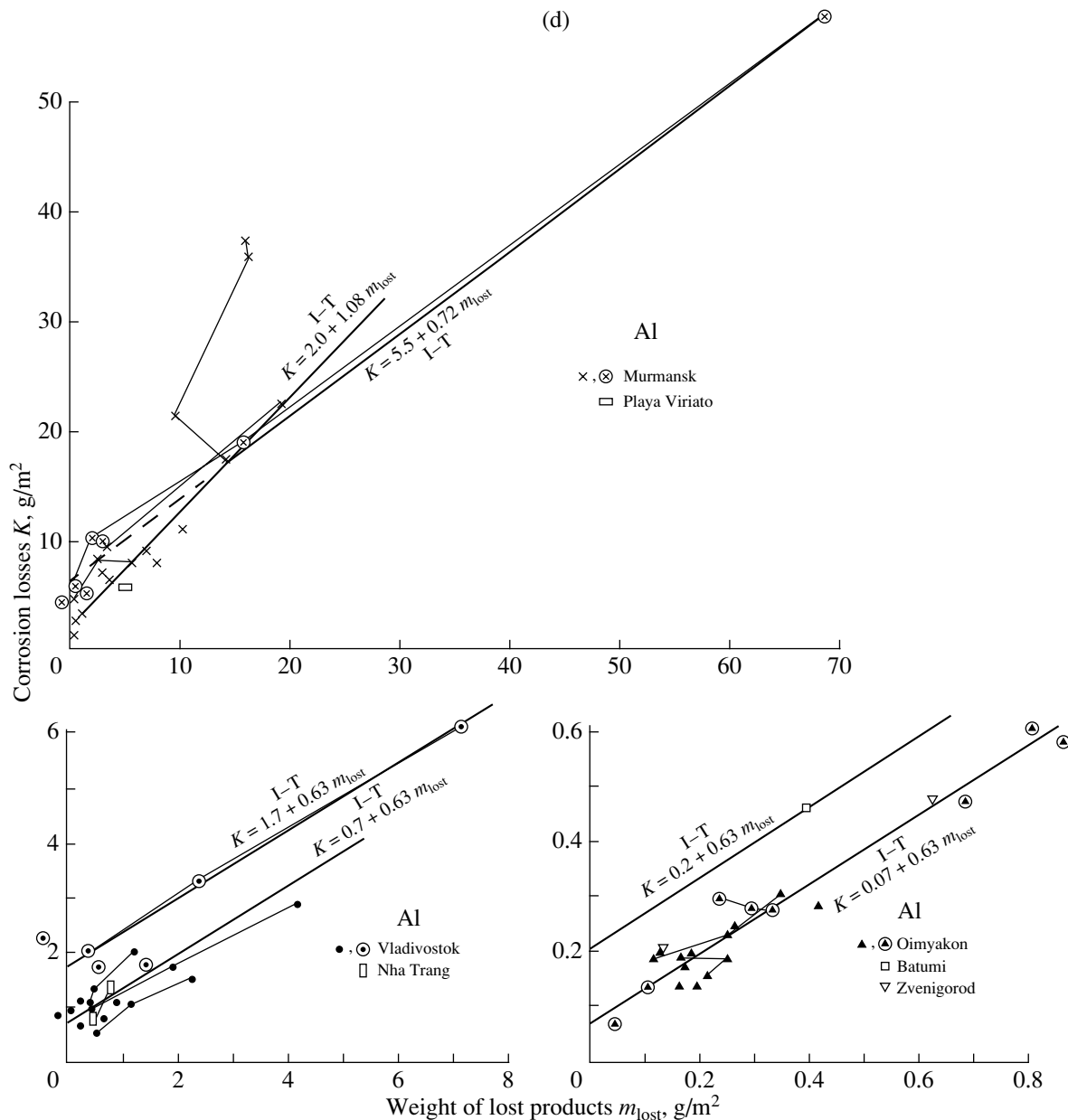


Fig. 7. (Contd.)

In the unpolluted atmosphere of Oimyakon (“the pole of cold” of the Earth), the transient stage lasts for more than 4 years. The largest k of 4.5 is calculated in Oimyakon for the unfinished incubation–transient stage. In Vladivostok, $k = 3.5$. This relatively large value is caused by the completion of the incubation–transient stage with an insignificant amount of the lost corrosion products.

At the steady-state stage of corrosion in Murmansk and Vladivostok, the calculated K_0 for spirals is higher than that for plates; however, at these stations, coefficients k are equal for both types of specimens indicating that the corrosivity of electrolyte layers on them differ

only slightly. Judging from k in Murmansk (0.78) and Vladivostok (0.48), the level of the atmospheric corrosivity in Murmansk is higher (a raised concentration of sea salts accumulated on the metal surface, low rain intensity). An increase in the corrosion losses is determined not only by coefficient k , but also by the discharge of products, which is clearly predominant in Vladivostok, especially on the wire spirals.

The values of k calculated by few available experimental data for Nha Trang (Vietnam) and Via Blanca (Cuba), are 0.74, whereas for urban and rural regions in Georgia and Russia (Batumi and Zvenigorod), in Cuba

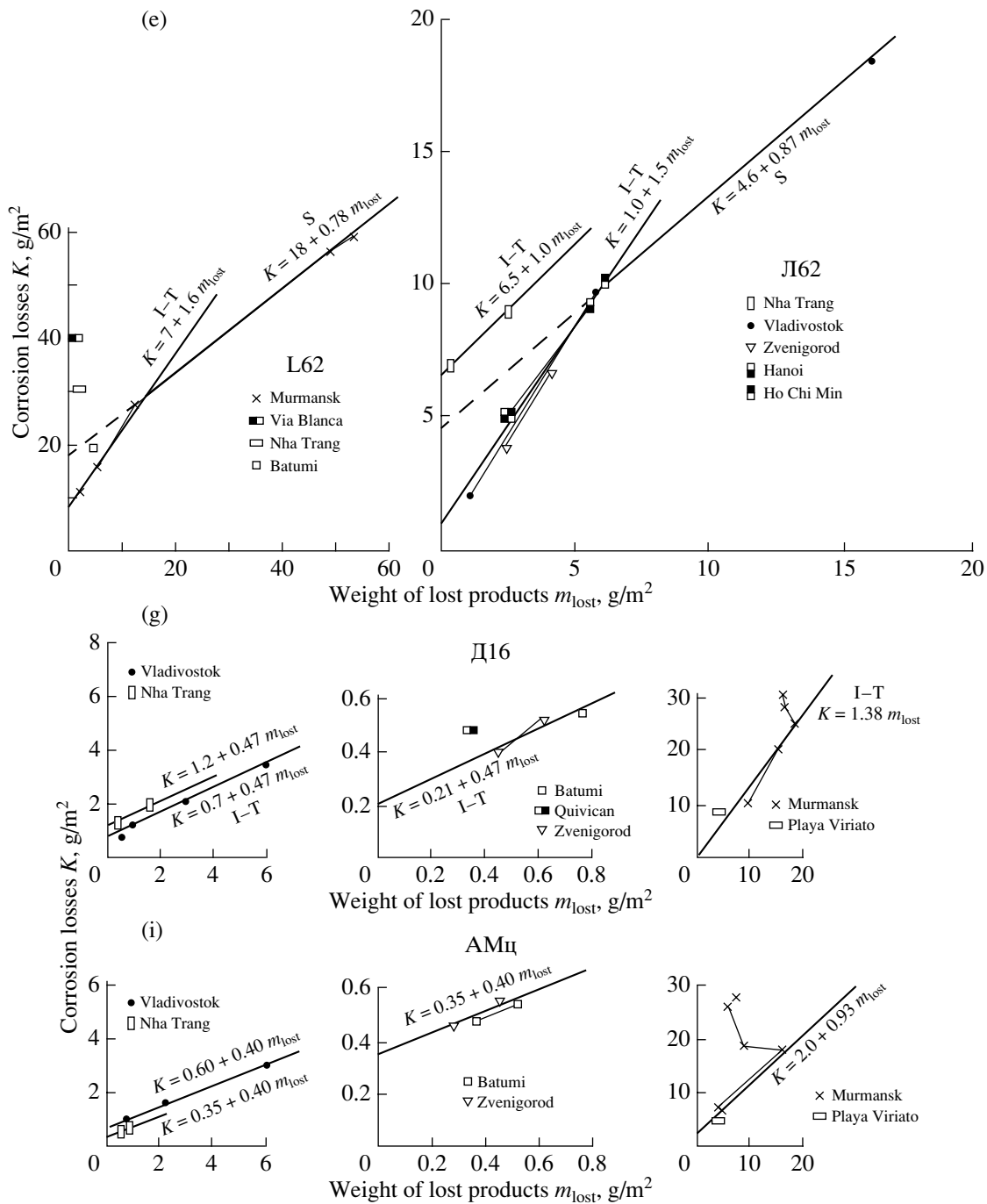


Fig. 7. (Contd.)

(Quivican), and in Vietnam (Hanoi, Ho Chi Min), $k = 0.60$.

Zinc, Fig. 7b. For zinc and other nonferrous metals, only the results of one-year tests were available. In Oimyakon, according to one-year data, we managed to recognize the general incubation–transient stage, whereas, in other regions, only the steady-state stage. In Oimaykon, the general stage corresponds to the corrosion losses of zinc up to 5 g/m² for the discharge of products to 3 g/m². For this period, K_0 and k are 0.6 and

1.68 g/m², respectively. In Vladivostok, for the steady-state stage of corrosion process, $k = 0.79$ on both, the plates and spirals, whereas K_0 is higher for spirals than for plates. In Murmansk, for plates $k = 1.35$; as regards other marine atmospheres, $k = 4.5$ in Nha Trang and $k = 14.0$ in Playa Viriato. In urban and rural regions, $k = 0.53$.

Copper, Fig. 7c. The incubation–transient stage on copper in Murmansk and Vladivostok lasted until the corrosion losses reached 40 and 27 g/m² for the dis-

Table 4. Calculated coefficients K_0 (g/m²) and k (g/m²) (the ratio of corrosion losses to the lost products) in the model equation $K = K_0 + km_{\text{lost}}$ for the incubation–transient (i-t) and steady-state (s) stages of corrosion process; *pl* are the plates, *sp* are the spirals

Station		Steel 3				Zinc				Copper			
		i-t		s		i-t		s		i-t		s	
		K_0	k	K_0	k	K_0	k	K_0	k	K_0	k	K_0	k
Vladivostok	<i>pl</i>	0	3.5	170	0.48	–	–	7	0.79	3.0	2.0	15	0.69
	<i>sp</i>	0	3.5	240	0.48	–	–	14	0.79	6.5	2.0	19	0.69
Murmansk	<i>pl</i>	0	2.5	80	0.78	–	–	5	1.35	9	2.0	25	0.88
	<i>sp</i>	0	2.5	190	0.78	–	–	11	0.91	9	2.0	25	0.88
Oimyakon	<i>pl</i>	0	4.5	–	–	0.6	1.68	–	–	0.3	2.0	–	–
	<i>sp</i>	0	4.5	90	0.60	0.6	1.68	–	–	0.6	2.0	–	–
Batumi	<i>pl</i>	0	2.0	90	0.60	–	–	5	0.53	2	2.5	–	–
Zvenigorod	<i>sp</i>	–	–	90	0.60	–	–	5	0.53	0	3.9	–	–
Hanoi	<i>pl</i>	–	–	90	0.60	–	–	5	0.53	2	2.5	–	–
Ho Chi Min	<i>sp</i>	–	–	90	0.60	–	–	5	0.53	2	2.5	–	–
Quivican	<i>pl</i>	–	–	90	0.60	–	–	5	0.53	0	3.9	–	–
Nha Trang	<i>sp</i>	–	–	0	0.74	–	–	0	4.50	0	2.1	–	–
Via Blanca	<i>pl</i>	–	–	0	0.74	–	–	–	–	–	–	–	–
Playa Viriato	<i>sp</i>	–	–	–	–	–	–	0	14.0	–	–	–	–
Station		Aluminum		Д16		AMц		Brass					
		i-t		s		(i-t) + s		i-t		s			
		K_0	k	K_0	k	K_0	k	K_0	k	K_0	k		
Vladivostok	<i>pl</i>	0.7	0.63	0.7	0.47	0.60	0.40	1.0	1.5	4.6	0.87		
	<i>sp</i>	1.7	0.63	–	–	–	–	–	–	–	–		
Murmansk	<i>pl</i>	5.5	0.72	0	1.38	2.0	0.93	7.0	1.6	18	0.78		
	<i>sp</i>	2.0	1.08	–	–	–	–	–	–	–	–		
Oimyakon	<i>pl</i>	0.07	0.63	–	–	–	–	–	–	–	–		
	<i>sp</i>	0.07	0.63	–	–	–	–	–	–	–	–		
Batumi	<i>pl</i>	0.2	0.63	0.21	0.47	0.35	0.40	–	–	–	–		
Zvenigorod	<i>sp</i>	0.07	0.63	0.21	0.47	0.35	0.40	1.0	1.5	–	–		
Hanoi	<i>pl</i>	–	–	–	–	–	–	1.0	1.5	–	–		
Ho Chi Min	<i>sp</i>	–	–	–	–	–	–	1.0	1.5	–	–		
Quivican	<i>pl</i>	–	–	–	–	–	–	–	–	–	–		
Nha Trang	<i>sp</i>	–	–	1.2	0.47	0.35	0.40	6.5	1.0	–	–		
Via Blanca	<i>pl</i>	–	–	–	–	–	–	–	–	–	–		
Playa Viriato	<i>sp</i>	–	–	–	–	–	–	–	–	–	–		

charge of the products of 10 and 15 g/m², respectively. In Oimaykon, even after 4 years (for $K = 2.2$ g/m² and $m_{\text{lost}} = 1$ g/m²), they were not yet finished. For these regions, coefficients k for plates and spirals are equal ($k = 2.0$), whereas K_0 is higher for spirals. Upon reaching the steady state of corrosion, in Vladivostok, k is equal for copper plates and spirals ($k = 0.69$), whereas K_0 is higher for the spirals. In Murmansk, due to a large

scatter of experimental data, no evident difference between the plates and spirals was found. Coefficient k , approximately estimated as 0.88, is higher than in Vladivostok, which indicates a higher corrosivity of the marine atmosphere of Murmansk to copper.

In other regions (Quivican, Hanoi, etc.), the experimental data is lacking. Based on the data for Vladivostok and Murmansk we can suppose that, during the incubation and transient stages, as a whole, the corro-

sion losses can be 27–40 g/m². In this case, the calculated magnitudes of k fall in a range of 2.1 to 3.9. They are higher than the calculated coefficients k for similar stages in Murmansk, Vladivostok, and Oimyakon; however, additional tests of copper are required to refine them.

Brass 62, Fig. 7d. In Murmansk, the incubation and transient stages on brass are completed when corrosion reaches 30 g/m² and the product loss is 20 g/m². In this case, $k = 1.6$ and $K_0 = 7.0$. In Vladivostok, this is reached at a corrosion of about 10 g/m² and $m_{\text{lost}} = 6$ g/m². The calculated k of 1.5 for Vladivostok is approximately equal to that for Zvenigorod and the stations in Vietnam except for Nha Trang ($k = 1.0$). The steady-state stage is characterized by smaller k : 0.87 in Vladivostok and 0.78 in Murmansk. For other stations, the data are lacking, and the coefficients were not calculated.

Aluminum, D16 and AMu Alloys, Figs. 7f and 7g. Both coefficients for these materials in the equations describing the corrosion process at the incubation–transient stages, as well as the steady-state stage, are identical. In Vladivostok, for aluminum plates and wire spirals, $k = 0.63$. The corrosion losses of aluminum, which are observed in Zvenigorod, Batumi, and Oimyakon, as well as in Vladivostok ($k = 0.63$) are relatively close. For the alloys, they also differ only slightly in different regions. The slopes of the straight lines corresponding to Eq. (6) for D16 and AMu alloys in all the regions (except for Murmansk and Playa Viriato) are almost identical (k , or the slope of the curves $\tan \alpha$, is 0.47 and 0.40).

In the marine atmosphere, aluminum and alloys are susceptible to pitting, whereas the alloys are also susceptible to a subsurface corrosion under a phase film of moisture containing dissolved sea salts. In Murmansk, the slope k (calculated from the corrosion weight losses) equals 1.08, 1.38, and 0.93 for plates of aluminum and alloys D16 and AMu, respectively. Unlike this, for aluminum wire spiral, $k = 0.72$. Due to a cylindrical surface, of the wire, even a drizzle can wash away from it accumulated sea salts, thus suppressing the intense corrosion.

When pitting has not yet developed, the linear $K = f(m_{\text{lost}})$ dependence for aluminum wire spiral is retained at least for the corrosion losses of up to 60 g/m² and the discharge of 70 g/m² products; for plates, it may be conventionally considered to be completed at $K = 20$ g/m² and $m_{\text{lost}} = 15$ g/m². With the further corrosion development, m_{lost} may not increase. On the contrary, it can decrease because of the pitting initiation, impediment of the dissolution, washing off, and weathering of the products. This difference in the behavior of aluminum plates and spirals is a clear evidence for the effect of the loss of the products on the corrosion development. For instance, in 8 years, under similar conditions, corrosion of spirals reaches 56 g/m², whereas corrosion of plates

is only 32 g/m², though, in this case, k characterizing the corrosivity of environment, is 1.08 for plates and 0.72 for spirals. This indicates that corrosion is severer, when the loss of the products is intenser.

The experimental data characterizing corrosion of the plates (aluminum, D16, and AMu) in Playa Viriato fall within the scatter of experimental results in Murmansk. This evidences the high atmospheric corrosivity in Playa Viriato; however, it is not higher than in Murmansk, although the air salinity in Playa Viriato is by an order of magnitude higher.

Thus, this experimental model (Eq. 6, Fig. 7) quantitatively describes the dependence of corrosion on the discharge of products and the corrosivity of medium on the metal covered with a layer of corrosion products. In every climatic zone studied, the discharge of products has a strong effect on the further spread of corrosion. Strictly speaking, the model can not predict the corrosion losses, because the m_{lost} parameter used in the model, is calculated (Eq. 5) from the known corrosion rate K . Yet, using the model and known coefficients K_0 and k , the weight of products lost both at the incubation–transient and steady-state stages of corrosion process, can be approximately estimated in the absence of quantitative data on the weight of corrosion products retained by the metal:

$$m_{\text{lost}} = (K - K_0)/k. \quad (7)$$

Undoubtedly, it is of great practical importance when solving environmental problems associated with the estimation of detrimental substances entering the environment with the corrosion products from the metal structures operated in open atmosphere.

CONCLUSIONS

(1) Protective properties of the products of atmospheric corrosion are not directly related to their weight but determined by their chemical and physical nature depending on aerochemical and climatic parameters of the environment affecting simultaneously the metal and its corrosion products. The previous mass of the products retained by the metal surface is gradually renewed. Their weight insignificantly increases in time and comprises an insignificant fraction of the total weight of corrosion products formed. By contrast, the weight of lost products increases and, actually, is the prevailing fraction of the products formed. Therefore, it may be considered as the predominant parameter characterizing atmospheric corrosion. The discharge of products promotes the further corrosion process.

Such parameters as the weight of retained products m (or their weight per unit corrosion loss m/K) are unsuitable when developing a practical mathematical model based only on these parameters. The weight of products lost from the metal surface during its life-time in the corrosion process, is more practicable as an important parameter of the model. Similar to the weight

corrosion losses of metal (which is determined by the intensity of weather factors and the corrosivity of impurities in the air), m_{lost} gradually or periodically increases with time.

(2) A mathematical model relating the corrosion to the weight of products, which are lost at the incubation–transient and steady-state stages of corrosion process, is considered. The coefficients of the model of estimating the corrosion of CT3, copper, brass, zinc, and aluminum, as well as its Д16 and АМц alloys, are determined in the zones of moderate, subtropical, and tropical climate.

(3) A model, which quantitatively relates the corrosion losses of a metal to the weight of the products discharged to the environment, can be useful (in the absence of quantitative data on the weight of the products retained on the metal) when estimating the amount of detrimental substances entering with the products into the environment in the course of the corrosion of metal structures operating in open atmosphere.

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