# THE CAUSE OF THE INHIBITING EFFECT OF HALIDE IONS ON THE DISSOLUTION OF IRON AND STEELS IN SULFURIC ACID

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Addition of halide ions to sulfuric acid slows down autosolution of iron and Fe-Cr and Fe-Ni alloys [1-5]. Polarization measurements show [4, 5] that this retardation of corrosion is chiefly due to an increase in the overvoltage of the cathode process. The authors of [4-8] indicate that there is a similar rise in the overvoltage of anode dissolution.

This change in the kinetics of cathode and anode processes is usually associated with formation of chemisorbed layers of halide ions on the electrode surface. This is supported by experimental data on adsorption of halide ions on an iron electrode [9].

However, the retardation of the anode process by halide ions is not observed in every case. The authors of [10, 11] found that in certain conditions these ions have no effect on the anode solution rate of iron. According to [12], addition of chlorides accelerates the anodic solution of stainless steel in sulfuric acid. This author studied the effect of bromide and iodide ions on the solution of steel, and found that at high ionic concentrations retardation of the anode process decreases with increasing concentration.

In [12] it was found that halide ions also have a marked effect on the passivation characteristics of iron and steel; the results of the research are therefore considered by the authors primarily from the viewpoint of the effect of halide ions on the metal's passivation tendency. It is supposed that bromide and iodide ions form chemisorbed layers and promote passivation, while chloride ions displace the passivating oxygen and therefore play an activating role. The decreasing inhibiting effect of iodide with increasing concentration is related to possible participation of anions in the elementary ionization act, thereby forming complex anions.

This explanation assumes that the influence of chemisorbed layers of halide ions is twofold, i.e., includes retardation and activation. The authors of [13] studied the reasons for the activating effect of these ions on passive metals. Their conclusions agree with those in [12]. The reason for the retarded solution of metals in the presence of halides is still unknown. Explanations of such retardation are usually based on the analogy between it and metal passivation. To give a satisfactory explanation we must obviously draw a distinction between the effect of the halide ions on the kinetics of metal solution in the active state, and their effect in the passive state. Some of our data on the kinetics of active solution of iron and steels in halide solutions indicate that the inhibiting effect of halide ions can be explained in another way.

In our work we used the potentiostatic method to record anode polarization curves on iron and steels 12Kh6 and 1Kh13 in pure halide solutions of different concentrations. The measurements were made in unsteady conditions, the mean rate of change of potential being 30 mV/min. Fig. 1 gives data for steel 1Kh13, obtained by measurements in HCl + KCl solution at pH 3.* It will be seen that where steel undergoes anodic polarization in a halide solution, there is a point in the active solution potential range at which solution increases with increasing chloride concentration. This gives grounds to suppose that the retarding effect of halides, observed by these authors, is due to the specific effect of sulfate ions, because their experiments were carried out in $H_2SO_4$ + halides.

To determine the part played by sulfate in active corrosion of iron and steels, we plotted their

* All potentials relate to a standard hydrogen electrode.

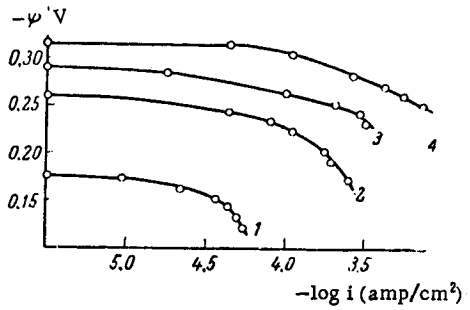


Fig. 1. Anode polarization curves, measured on steel 1Kh13, in HCl + KCl solutions at pH 3 and chloride concentrations (g. equiv/liter): 1) $10^{-3}$; 2) $5 \cdot 10^{-3}$; 3) $5 \cdot 10^{-2}$; 4) $5 \cdot 10^{-1}$ (Negative potential indi-indicated).

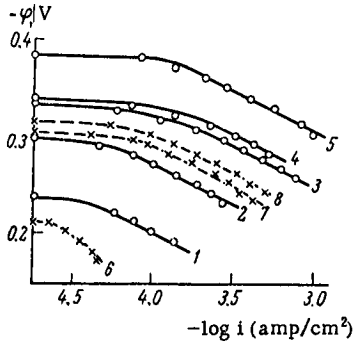


Fig. 2. Anode polarization curves (1-5), measured on steel 1Kh13, in $H_2SO_4$ + $Na_2SO_4$ solutions at pH 3 and sulfate concentrations (g. equiv/liter): 1) $10^{-3}$; 2) $10^{-2}$; 3) $5 \cdot 10^{-2}$; 4) $10^{-1}$; 5) 1. Curves 6-8 ditto for $H_2SO_4$ + KCl at pH 3 and chloride concentrations: 6) $10^{-2}$; 7) $10^{-1}$; 8) 1 N.

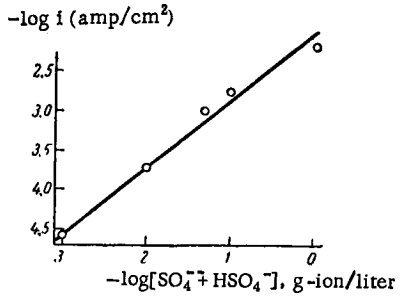


Fig. 3. Dissolution rate of steel 1Kh13 at potential -0.25 V in solution of $H_2SO_4 + Na_2SO_4$ at pH 3, at pH 3, plotted versus sulfate concentration.

polarization curves in pure sulfate solutions of different concentrations ($H_2SO_4$ + sodium sulfate). It was found that, like halide ions, the $SO_4$ anions promote active corrosion of iron and steels.* Fig. 2 (curves 1-5) plots the corresponding data for steel 1Kh13. Fig. 3 plots the corrosion rate of steel at constant potential (-0.25 V) versus sulfate concentration†; it will be seen that with a tenfold increase in sulfate concentration, dissolution of steel 1Kh13 is accelerated by a factor of ~10. The accelerating effect of the sulfate was also found in our work on the corrosion of iron and steel 12Kh6.

A comparison of Fig. 1 and 2 gives grounds to suppose that in these conditions sulfates have a greater accelerating effect on steel than chlorides; at the same anion concentration in the solution, the corrosion rate of steel is lower in chlorides than in sulfates.

Leaving aside the character of the elementary stages in solution of iron and steels in halide or sulfate solutions, it is safe to assume that the promoting effect of these ions is related (like their influence on ionization of indium from an amalgam [14]) to their participation in the corrosion reaction.‡ We may thus assume that the corrosion velocity of metal during participation of $SO_4^{--}$ and $Hal^-$ ions (which have different accelerating effects) will depend on their surface concentrations. It follows that the resistance of iron and steel in a solution containing both types of ion will be governed by their relative content of these

* It is not strictly true to say that $SO_4^{--}$ ions usually promote corrosion because in the case of sufficiently acid solutions the effect may be due to $HSO_4^-$ ions. However, the character of sulfate activator particles is outside the scope of the present paper; here and below we will refer to these particles as sulfates or $SO_4^{--}$ ions.

† In cases where at −0.25 V the anode polarization curves deviated from the Tafel' relation, extrapolated current densities were used.

‡ These data cannot help to determine the nature of the elementary events on which iron and steel corrosion is based in sulfate and halide solutions, because they were obtained without a constant ionic strength in the solution. Determinations of the $\psi_1$-potential in these conditions are insufficiently accurate. However, approximate determinations confirm the acceleration of metal corrosion by these anions.

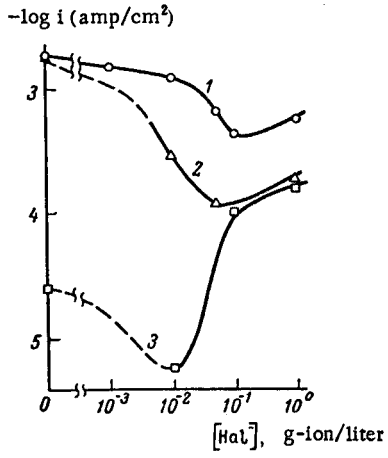


Fig. 4. Dissolution rate of steel 1Kh13 at constant potential (-0.25 V) in sulfuric acid solution, plotted versus concentration of added halide ions: 1) $10^{-1}$ N $H_2SO_4$ + KCl; 2) $10^{-1}$ N $H_2SO_4$ + KBr; 3) $10^{-3}$ N $H_2SO_4$ + KCl.

ions on the surface of the metal: this in turn is determined by the adsorbability of the anions and their volumetric concentration.

We may assume that addition of a small amount of halide ions to an $H_2SO_4$ solution will displace the sulfate ions (which are stronger activators of the anode process) away from the metal surface, thereby retarding dissolution owing to the participation of the $SO_4^{--}$ ions. This effect should increase with the halide content, but where the latter is very high the effect may be reversed, due to predominance of the dissolution reaction with participation of halide ions (this reaction velocity increases with the halide concentration).

This would explain the data [2, 3, 12] on the effect of halide ions on solution of iron and its alloys in sulfuric acid. We obtained stationary anode polarization curves for steel 1Kh13 in a 0.1 N $H_2SO_4$ solution with and without addition of chloride and bromide. It was found that addition of halide ions to an $H_2SO_4$ solution retards the autocorrosion of steel, the effect increasing with the halide concentration. But when the critical halide concentration is exceeded, the effect is reversed, i.e. an increase in the anion concentration increases the solution rate (Fig. 4, curves 1 and 2).

When curves 1 and 2 are compared, it is clear that halide retardation of metal solution in sulfuric acid depends markedly on the nature of the halide ion. Moreover, the quantitative differences in the promoting effect of sulfate and chloride ions on the solution kinetics of different metals (iron and steels) give grounds to suppose that this retardation is also related to the nature of the metal itself. Finally, the concentrations of sulfate and other ions capable of adsorption and of taking part in corrosion are obviously important.

By way of corroboration, chloride and bromide ions (from $10^{-4}$ to $5 \cdot 10^{-2}$ N) had no retarding effect on active corrosion of iron in 1 N sodium sulfate or on steel 12Kh6 in 0.1 N sulfuric acid. It is known that halide ions display maximum inhibiting properties in concentrated (up to 10 N) sulfuric acid [1, 2, 4]. Since the promoting effect increases with the sulfate ion concentration, the retardation effect, which is related to displacement of these ions from the surface of the metal, should likewise increase with the sulfate content in the solution.

The decrease in this inhibiting effect in dilute sulfate solutions may also be due to the fact that with a constant halide concentration in the solution the $Hal^-/SO_4^{--}$ concentration ratio will increase markedly. Dissolution with participation of halide ions thus becomes predominant, even at fairly low $Hal^-$ concentrations. This is illustrated by measurements in sulfuric acid with added chloride ions at pH 3 (cf. Fig. 1, curves 6-8, and Fig. 4, curve 3). It follows that in this case the inhibiting effect only occurs where the $Cl^-$ concentration is less than $10^{-2}$ N; at higher concentrations the inhibition is replaced by promotion.

It should be noted that according to the mechanism suggested by the authors of [15, 6, 7], in active dissolution of iron hydroxyl ions take part in the elementary act of ionizing the Fe atoms. This mechanism is based on experimental data for solutions with constant sulfate concentration. If our data for different sulfate concentrations are taken into account, it would appear that the process is rather more complex. A very definite role is played by the $OH^-$ ions as well as the sulfate ions. This means that in studying the effect of halide ions on the dissolving of metal in sulfate solutions, we must bear in mind that these ions displace $OH^-$ ions as well as $SO_4^{--}$ ions. We should expect that the retardation effect will depend on the acid number of the solution. This is confirmed by the author of [16], who shows that the inhibiting effect of iodide on the self-corrosion of iron in a sulfate solution is heightened when the solution pH is reduced.

Our work has shown that when solution-activating particles are added to a solution containing metal-corrosion promoters whose particles have stronger promoting effects than the added particles, the process can be slowed down by adsorptive displacement of the more active particles by the less active ones. The effect associated with this depends on the concentration of the corrosion-promoting particles in the solution and their adsorption capacities.

## SUMMARY

Chloride and sulfate anions accelerate the active dissolution of iron and steels insofar as they take part in the corrosion process. Where sulfates take part in the reaction, solution is more rapid than for halide-ion participation. The inhibiting effect of halide ions on solution of iron and steels in sulfuric acid is explained by displacement of the more active sulfate ions from the surface of the metal by the halide ions. In accord with this explanation, the inhibiting effect of halide ions is only displayed where their concentration is below a critical value; beyond this point, an increase in concentration is accompanied by weakening of the inhibiting effect, or faster solution than in pure sulfuric acid.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.

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