HETEROGENOUS ISOTOPIC EXCHANGE AT THE INTERFACE OF STEEL SHEETS IN CONTACT WITH IRON CHLORIDE SOLUTIONS

II. EXPERIMENTS WITH IRON(III) CHLORIDE AND IRON(II) AMMONIUM SULFATE SOLUTIONS

By

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(Received October 7, 1968)

The first part of this paper [1] dealt with the surface preparation and surface qualification of steel sheets, used in our heterogenous isotopic exchange investigations. It tried to define the metal surface with regard to purity and the actual surface, to render thereby the evaluation of exchange processes possible.

This paper reports on the isotopic exchange experiments undertaken.

Experimental part

The plates, adequately prepared, were placed into 5 to 10 ml of aqueous ferric chloride or ferrous ammonium sulfate solution containing ^{55}Fe ions. Under intensive stirring of the solution, the isotopic exchange during various times of investigation was determined with an apparatus Model EKCO, using NaI(TI) X-ray crystal for detection. (Applied voltage 1150 V, at a discriminator bias of 10 V, measuring time 100 s, amplifier gain: 100×.)

^{55}Fe (^{59}Fe) isotope was used for the experiments in form of $FeCl_3$ in 0.2 molar HCl solution. The specific activity of this solution was 20.5 mCi/gFe (5.4 mCi ^{59}Fe/gFe). 15 ml of this solution diluted to 50 ml represented that stock solution, with which the inactive solutions have been traced. Generally 0.001 or 0.1 m $FeCl_3$ or $Fe(NH_4)_2(SO_4)_2$ solutions were used as inactive solutions.

The detection of the 5.9 keV X-ray radiation of Fe^{55} ions of a half life of 2.7 years with GM counter and with scintillation γ-crystal is of poor efficiency. We tried therefore a scintillation X-ray crystal and a through-flow GM counter for measuring the activity of the X-ray radiation. Our experiments showed the first approach to be more suitable. Further possibilities, such as a plastic scintillator or the measurement of the 1.1 MeV radiation of ^{59}Fe were not investigated.

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Activity was measured on both sides of the plate, and, under consideration of the decrease in radiation caused through absorption by the plate of given thickness, the actual activity on both sides of the plate has been calculated. First, this value was referred to the unit of geometrical surface (1 cm^2), then the roughness factor of the surface measured was taken into account. Fe equivalents in mg, corresponding to the activity measured, were determined under identical experimental conditions by analytical methods.

Rejection of doubious values

As shown by way of example in Table I. the rejection of intensity measurements data was decided on the basis of the Chauvenet criterion. Intensity measurement was considered as »good«, if data obtained from 3 or 5 measurements fulfilled the Chauvenet criterion.

Table I

Application of the Chauvenet criterion

$\bar{n}$	n	$n-\bar{n}$	f	Note
1418	1416	− 2	1.42	good series ($c_5=1.64$)
	1440	22		
	1364	54		
	1443	25		
	1426	8		
1424	1440	16	1.06	good series ($c_3=1.4$)
	1387	−40		
	1446	22		
479	457	−22	1.0	good series ($c_5=1.64$)
	484	5		
	491	12		
	488	9		
	476	− 3		

$$f = \frac{n-\bar{n}}{\sigma} \qquad \sigma = \bar{n} \qquad c_5 = 1.64$$

(c_5 is the value of the Chauvenet criterion, read from the diagram for 5 measurements)

Limit of detection

In course of the detection of ^{55}Fe radiation with an X-ray crystal, the increase in radiation with increasing Fe ion concentration was investigated (Table II). The data are reliable, so that it can be accepted as detection limit, if the level increases by 20 per cent of the background (which maximum

Table II

The intensification of the radiation for increasing Fe ion concentrations

Fe (mg) (a)	n_k (b)	$\frac{b}{a} \cdot 10^{-3}$
$1.68 \cdot 10^{-1}$	36.676	219
$1.68 \cdot 10^{-2}$	4.310	257
$8.40 \cdot 10^{-3}$	2.059	245
$3.36 \cdot 10^{-3}$	888	264
$8.40 \cdot 10^{-4}$	232	276

is 460 cpm), that is to say, by 100 cpm. The quantity of iron corresponding to this value is:

$$x_m = \frac{5 \cdot 10^3 \cdot 100}{1375} \; 3.6 \times 10^{-4} \, \mathrm{mg} \;\; \mathrm{Fe}/100 \; \mathrm{cpm}.$$

This corresponds to 4×10^{15} Fe atoms.

The rejection of the measurement data of the actual exchange

After deciding on the rejection of the results obtained in the intensity measurements for each specimen, the evaluation of the reliability of surface isotope exchange data, calculated from these results, poses further problems. The degree of reliability is influenced by several factors, thus e.g. by the roughness of the surface, discussed in our previous communication [1], by the concentration, pH and temperature of the solution, by the efficiency of rinsing, i.e. the quantity of ions adsorbed on the surface. These variables can be taken into account and fixed only to a certain extent.

The efficiency of rinsing, or better the quantity of ions adsorbed on the surface of germanium has been already investigated in this Institute [14]. According to these investigations and other pertinent data in the literature, in the case of adequate rising a monomolecular adsorbed ion layer, that is to say, a quantity of about 10^{15} ions/cm^2 is to be expected. (In the case of K^+ ions and Ge surface, the adsorption of $1 - 5 \times 10^{13}$ K^+ ions per each cm^2 is the most probable value.)

A time of the order of 60 minutes is required for the adsorption equilibrium to establish.

Before the actual measurements, the test specimens were rinsed for 1—2 minutes in distilled water, and then dynamically sprayed with a water jet for 2—3 minutes and dried. Thus, the source of error, due to adsorbed Fe ions, could be minimized.

Evaluation of experimental results

Some experimental results are shown in Tables III to XXI. These tables contain data on the solutions used in the experiments, the geometry of the plate used, exchange times, the activity measured and that referred to unit surface, the exchanged quantity of Fe in mg, referred to the geometrical surface, data on the fineness of the surface of the plate used (measured Ra value, calculated roughness factor), and Fe exchange in mg referred to the actual surface. Under consideration of these factors, in 0.5 to 30 minutes 0.1 to 1.5 × 10^{-4} mg of Fe is exchanged on the actual surface. (1×10^{-4} mg of Fe corresponds to $1.08 \cdot 10^{15}$ atoms.)

Table III

Isotopic exchange in 0.001 molar $FeCl_3$ solution
Solution: 20 ml of 0.001 m $FeCl_3$ + 0.17 ml of active $FeCl_3$
Activity of the solution: 1.23×10^6 $3.32 \cdot 10^5$ c/100s; c/100s/mg Fe

Plate No.	Geometrical surface (cm²)	Time of exchange (investigation)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange referred to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Remark
1.	2 · 2.55	50 sec	874 879	232 232	7	0.85	28	0.25	
1/a	2 · 2.55	0.5 min	827 756	187 137	5.6 4.1			0.20 0.14	
		6 min	1419 1419	375 375	11.3			0.40	
2.	2 · 2.8	50 sec	629 635	150 155	4.5	0.45	15	0.30	
2/a	2 · 2.8	0.5 min	540 556	112 124	3.4 3.7			0.23 0.25	
		6 min	1425 1432	342 348	10.2			0.68	
3.	2 · 2.8	0.5 min	394 394	96 96	2.9	0.75	24	0.12	
4.	2 · 2.55	0.5 min	525 525	140 140	4.2	0.30	10	0.42	

For a further evaluation, the number of the Fe atoms (ions) on 1 cm² of the actual surface has to be determined. Starting from the body-centered lattice structure of steel, and taking as the atomic diameter of Fe 2.5Å, the space requirement of one atom will be $\frac{3\times/2.5\times10^{-8}}{2} = 5.4\times10^{-16}$ cm².

Therefore, $1/5.4 \times 10^{-16} = 1.85 \times 10^{15}$ Fe atoms/cm² will be accomodated on 1 cm² of the actual steel surface. According to this calculation, for the total exchange of the atoms on 1 cm² of surface 1.7×10^{-4} mg of Fe/cm² is necessary. Values obtained in our investigations are generally below this value. Also measured data shown in Fig. 1 prove that in 30 minutes the exchange is

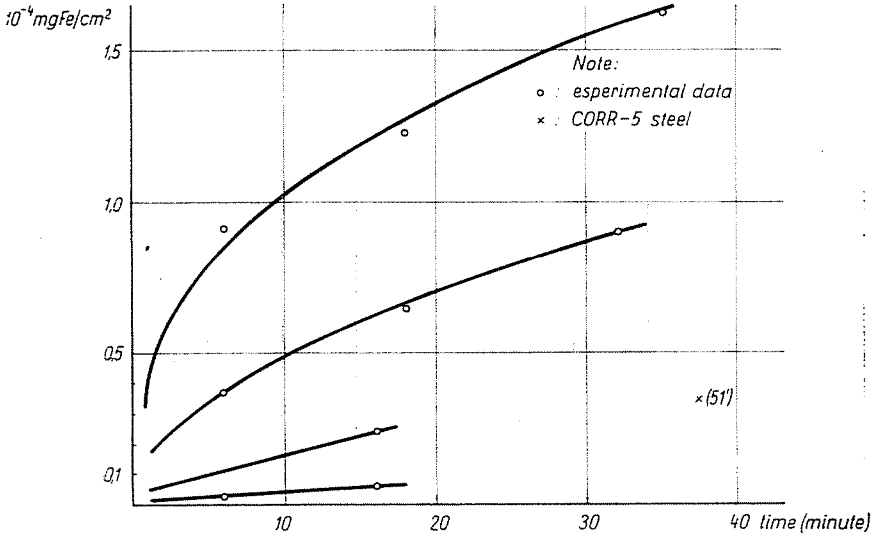

Fig. 1. Isotope exchange measured on the surface in function of exchange time

Table IV

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 20 ml of 0.001 m $FeCl_3$ + 0.15 ml of active $FeCl_3$
Activity of the solution: 1.23×10^6 c/100s

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange referred to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)
5	2 · 2.4	1 min	458 368	152 81	4.6 2.4	0.93	31	0.15 0.08
		2 min	935 907	272 245	8.2 7.4			0.26 0.24
		4 min	1424 1400	407 387	12.2 11.7			0.4 0.38
6	2 · 2.7	1 min	692 702	174 177	5.3			Plate treated with cc HNO_3 for 1 min

Table V

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 10 ml of 0.001 m $FeCl_3$ + 0.07 ml of active $FeCl_3$
Activity of the solution: 5.32×10^5 c/100 s

Plate No.	Geometrical surface (cm²)	Time exchange (investigation)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)
7	2 · 1.1	27 min	1670	1040	22.4			the plate decolourized, became „rusty"
			1670					
			1260	680	14.6			Decolourization, „rust" removed
			1418	960	20.5			
		10 min	1211	722	15.5			
			1272	800	17.2			
			277	120	2.6			Surface layer dissolved in 1 : 1 HCl, 30 sec
			363	273	5.9			
			129	74	1.6			Etched in 1 : 1 HCl, 30 sec

Table VI

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 10 ml of 0.001 m $FeCl_3$ + 0.12 ml of active $FeCl_3$
Activity of the solution: 1.25×10^6 c/100s

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)
8	2 · 1	33 min	5048	3570	76			the plate decolourized, corroded
			4792	3080	66			
		73 min	72.019	49.500	1050			
			70.713	46.963	995			

about 80 per cent of the total exchange of the calculated surface. Presumably, the exchange proceeds at the active sites of the surface, repeatedly mentioned in the literature on adsorption.

This statement is contrary to the opinion, stated also in the book of HAISSINSKY [8], according to which, notwithstanding the small self-diffusion a relatively great number of atomic layers participate in the exchange. For example, in the 0.001 molar solutions of most of the metals several times 10 atomic layers participate for about 10 minutes in the exchange, and several

Table VII

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 10 ml of 0.001 m $FeCl_3$ + 0.10 ml of active $FeCl_3$
Activity of solution: 9.91×10^5 c/100s; 4.65×10^5 c/100s/mg Fe

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)
9	2.1	7 min	680 786	460 565	9.9 12.1			N_2 introduced during exchange into the solution
			600	400	8.6			Decolourization wiped off
			276 252	201 155	4.3 3.3			Decolourization polished off

Activity of the solution: 9.58×10^5 c/100 s

		10 min	816 766	590 483	12.7 10.4			
			734 720	463	9.9			Decolourization partly wiped off
			198	125	2.7			Etched in 1 : 1 HCl, 30 sec
			67	42	0.9			Etched in 1 : 1 HCl, 30 sec

hundred, if the solution concentration is 10 times higher. After the initial exchange, the process slows down, and becomes „irreproducible". The exchange of 10 and 100 surface atom layers has been observed by several authors, without however giving a logical explanation of the phenomenon, or eliminating the inconsistency with the known fact that the self-diffusion of metals is very low at this temperature (Table 21). Concerning the rate of heterogeneous exchange processes, HAISSINSKY [8] mentions that the rate determining step is either the exchange process proper, or the diffusion of one of the components. If one of the components is a solid, the overall rate will be determined usually by the self-diffusion. (Investigations of WAGNER, ZIEMENS.)

Why would the case of metal surfaces be exceptional?

At room temperature, atomic translations in solids are determined essentially by the degree of irregularities, i.e. by the number and presence

Table VIII

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 20 ml of 0.001 m $FeCl_3$ + 0.15 ml of active $FeCl_3$
Activity of the solution: 1.23×10^6 c/100 s

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured ($c/100s$)	Activity calculated ($c/100s$)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)
10. (CORR-5)	2×3.05	0.5 min	232 232	51	1.5	0.58	19	0.08
		8.5 min	375 351	79	2.4			0.12
Activity of the solution: 6.7×10^5 c/100s Solution: 10 ml of 0.001 m $FeCl_3$ + 0.08 ml of $FeCl_3$								
11. (CORR-5)	2×0.9	51 min	170 143	148 89	4.5 2.7	0.42	14	0.32 0.19
		6 h	216 169	194 95	5.8 2.9			0.41 0.21
Solution: see that of plate No. 10								
12. Glass plate	2×4.5	1.5 min	252 263	37 39	1.1 1.2			

of lattice defects according to SCHOTTKY and FRENKEL [8]. Neither can this be the explanation for the exchange of several times 10 or 100 atomic layers.

According to ERBACHER, the exchange is confined to a single atomic layer, if the metal has been kept previously in an identical solution. According to Haissinsky, this may diminish, or alternatively, increase the exchange [8].

IMRE [7] explains the phenomenon by the so-called pseudo-diffusion mechanism. According to this concept, at certain spots of the surface ions are formed and as a process opposite to dissolution, also ion adsorption, and precipitation by ion capture, incorporation takes place. In this way, it can be assumed that the tracer atom gets into the atomic layers of the deepler lattices of the metal surface. This concept gives an explanation for the phenomenon observed, it may be assumed, however, that the structure of the layer formed in the secondary process is different from the original structure of the metal. In this case, no isotope exchange on the surface can be spoken of since an isotope layer comented out is present.

In our investigations, the attack on the metal surface soon begun due partly to the strong acidity of the solution. In 10 to 15 minutes, visible discol-

Table IX

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 5 ml of 0.001 m $FeCl_3$ + 0.1 ml of active $FeCl_3$
Activity of the solution: 1.04×10^6 c/100s; 5.38×10^5 c/mg Fe

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Remark
13	2×2.27	0.5 min	130	91	0.75	0.25	8	0.09	
		1 min	223 195	119 143	0.98 1.17			0.12 0.15	
		2 min	522	366	2.95			0.37	
		4 min	524	368	3.12			0.39	
		9 min	733	520	4.26			0.53	
		36 min	1209 1017	950 589	7.8 4.8			0.98 0.60	
			96	68	0.56				Etched in 1 : 1HCl, 10 sec

Table X

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Remark
13/a	$22 \times .27$	1 min	298 437	160 353	1.3 2.9				Pretreatment: 1 : 1 HCl, 3 min
		26 min	632 806	340 680	2.8 5.6				
		86 min	1387 1438	980 1150	8.0 9.4				
		206 min	2230	1570	12.8				

Table XI

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 5 ml of 0.001 m $FeCl_3$ + 0.1 ml of active $FeCl_3$
Activity of the solution: 9.10×10^5 c/100s; 4.98×10^5

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)
14	2×2.27	0.5 min	127 177	67 146	0.6 1.3			Pretreatment: in 10 ml of 0.001 m $FeCl_3$, 1 hour
		1 min	248 217	190 132	1.7 1.2			
		2 min	294	206	1.8			
		8.5 min	635 465	510 280	4.5 2.4			
		24.5 min	753 675	582 322	5.2 2.9			Oxidized, decolourized surface
			274 244	208 153	1.8 1.4			Etched in 1 : 1 HCl, 5 min
			120	85	0.75			Etched in 1 : 1HCl, 3 min
		12 min	441 415	319 276	2.8 2.4			

ouration, a corroded layer was formed on the surface. Therefore, surfaces worked mechanically, change quickly, owing to dissolution and etching, so that the surface isotope exchange of plates kept longer in the solution, was difficult to evaluate. In our measurements, we tried to remove these surface formations. Else (e.g. in Tables 19 and 20), exchanges involving several atomic layers are to be expected. The dissolution of the surface in the test solution can have either of two effects: it may a) smoothen or b) coarsen the surface. This circumstance may be important for the evaluatuion of results shown in Table 16. With longer contact periods, the difference between the roughness factors decreases, partly explaining for the great difference between the actual exchanges. Though investigations described in the literature referred also almost without exception to acid solutions, little consideration was given to the effect of these solutions on the metal surface except the statement that in general, the rate of the exchange increases with increasing acidity.

Table XII

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 10 ml of 0.001 m $FeCl_3$ + 0.2 ml of active $FeCl_3$
Activity of the solution: 1.68×10^6 c/100s; 4.98×10^5 c/100s/mg Fe

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Remark
15	2×2,27	0.5 min	127	65	0.6	0.67	22	0.03	
			175	145	1.3			0.06	
		1 min	308	248	2.2			0.10	
			242	133	1.2			0.05	
		2 min	383	269	2.4			0.11	
		7 min	598	370	3.3			0.15	
			712	550	4.9			0.22	
17	2×2,27	0.5 min	124	68	0.6				Plate coated with sulfur-oxide layer!
			154	126	1.2				
		1.5 min	221	134	1.2				
			254	198	1.7				
		6.5 min	204	142	1.25				
		36.5 min	330	194	1.7				
			383	300	2.7				
		2 h	640	190	1.7				
			1111	1040	9.2 5.4				

The corrosion of metals is not a necessary precondition of the exchange, nevertheless, it favours the process by the „disintegration" of the surface. It follows from all this that some kind of „decomposition", loosening up, of the metal surface would be the possible explanation for the apparent multilayer exchange, while on the metal surface exhibiting the original metallic structure the surface layer can only take part in the exchange. This assumption seems to be supported by the fact that the exchange rate is also affected by the nature of the anions. The exchange is accelerated by a chemical effect of the anion on the metal [8]. The investigations of SCHWABE [12] on anion adsorption serve as indirect proof. According to these investigations, the probable reason of the slow uptake of anions by metal surfaces (Pt, Ni, Fe) may be the penetration of the anions into the "interior" of the metal, which proceeds along the crystal grain border. When SO_4^{2-} ions are adsorbed on nickel sheet, the sheet with the finest crystal grains exhibits the greatest adsorption. Adsorption on the border of the crystal grain was made visible by autoradiography. According to these findings, if the "penetration" of anions and the

Table XIII

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 10 ml of $H_2O + 0.3$ ml of active $FeCl_3$
Activity of the solution: 2.82×10^6 c/100s; 6.40×10^5 c/100s/mg Fe

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2		Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Remark
18/a	2×2.27	0.5 min	886 820	660 640	4.55 4.42	4.5	0.15	5	0.9	Polished
18/b	2×2.27	0.5 min	1105 1133	742 821	5.12 5.66	5.4	1.6	53	0.1	Lapped
18/a		1 min	1406 1224	1100 742	7.60 5.12	6.4			1.3	
18/b		1 min	1665 1744	1100 1280	7.60 8.84	8.2			0.15	
18/a		3 min	3543 2967	2820 1720	19.45 11.90	15.7			3.1	
18/b		3 min	3587 3675	2460 2630	17.0 18.15	17.6			0.32	
19	2×2.27	0.5 min	536 697	376 500	2.59 3.45					Polished (one side), lapped (other side)
		1 min	1105 1235	780 880	5.39 6.06					

"penetration" of several atomic layers of isotope into the metal surface is accepted, this also means that a structural decomposition or transformation of the metal surface must be assumed, which can be considered as the beginning of corrosion process.

In our investigations, no significant or evaluable difference was found between the isotope exchange in ferric chloride solutions and that in ferrous ammonium sulfate solutions. (Roughness factors of adjacent surface areas of 1 cm^2 of a given plate, are more different.) Presumably, in the true surface isotope exchange the role of the anions is unimportant.)

When plotting our measuring results (Fig. 1), and connecting values belonging together, curves of the same shape are obtained, as those measured by. Imre [7] in the exchange of ^{111}Ag ions on a silver surface, and in that of ^{64}Cu ions on copper surface.

Table XIV

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 20 ml of 0.001 m $FeCl_3 + 0.2$ ml of active $FeCl_3$
Activity of the solution: 1.28×10^6 c/100s; 3.00×10^5

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ Fe/cm^2)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ n g Fe/cm^2)
21/a	2×2.73	1 min	142	86	1.05	0.64	21	0.05
21/b	2×3.1	1 min	148 200	45 166	0.5 1.8	2.7	90	0.02
21/a		6 min	294	178	2.2			0.1
21/b		6 min	442	270	2.9			0.03
21/a		16 min	686	400	4.9			0.24
21/b		16 min	1110	500	5.4			0.06
21/a 21/b		76 min	614 626 1200	400 540	4.9 5.8			0.24 0.064
21/a		256 min	540 600	400	4.9			0.24
21/b		256 min	1505 1620	785 1110	8.45 11.95			0.11

The exchange process time can be described by the empirical kinetic equation

$$\lg x = a \cdot \lg t + b,$$

where x is the exchange of Fe ions referred to unit surface, t is the time of exchange, and a and b are constants depending on the system (Fig. 2). A similar relationship was obtained on lead surface for the exchange of lead ions in 10^{-3} m $PbCl_2$ solution (pH 5.05) at various temperatures, and in the exchange Bi/Bi^{3+} in the bismuth salt solutions of various anions (Cl^-, NO_3^-, SO_4^{2-}) [8].

Presumably, the rate determining step is the liquid phase diffusion (ion diffusion). This is supported by the results of experiments in otherwise identical conditions, in which smooth and rough plates were placed simultaneously into the solution (see e.g. Table 16). Owing to the almost four times as great actual surface area (having presumably a proportionally greater number of active spots), it was to be expected that in these experiments the

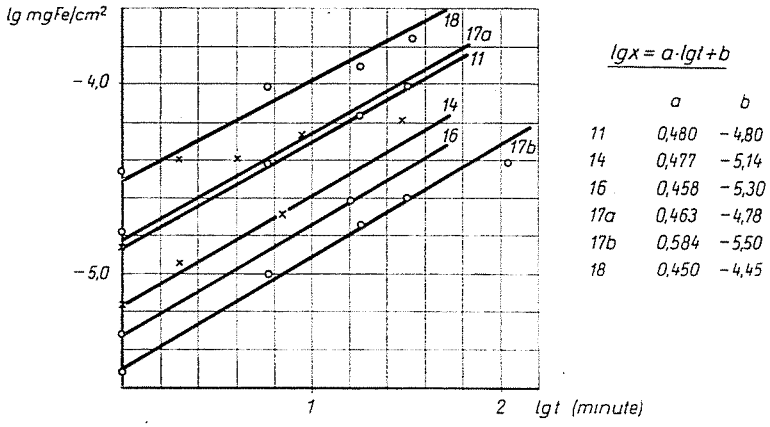

Fig. 2. Log diagram of the isotope exchange on the surface vs. exchange time

Table XV/a

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Solution: 20 ml of 0.001 m $FeCl_3$ + 1 ml of active $FeCl_3$
Activity of the solution: 4.97×10^6 c/100s; 3.00×10^5 c/100s/mg Fe

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)
22/a	2×3.12	1 min	540 460	410 186	4.4 2.0 3.2	0.64	21	0.16
22/b	2×3.26	1 min	445 537	164 431	1.7 4.8 2.8	2.7	90	0.03
22/a		6 min	1180 1025	960 400	10.3 4.3 7.3			0.35
22/b		6 min	1510 1543	900 920	9.2 9.4 9.3			0.10
22/a		18 min	1992 1714	1440 880	15.4 9.5 12.8			0.64
22/b		18 min	2420 2472	1460 1490	14.9 15.2 15			0.17
22/a		32 min	2590 2185	2040 890	21.8 9.5 15.7			0.78
22/b		32 min	3341 3176	2260 1700	23.1 17.4 20.2			0.22

Table XV/b

Isotopic exchange in 0.001 molar $FeCl_3$ solution

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Remark
22/a		124 min	3522 3472	2180 2100	23.3 22.6 22.9			1.14	
22/b		124 min	4735 4472	3200 2380	36.0 24.2 30.1			0.33	
22/a		259 min	4743 4429	3100 2475	33.2 26.4 29.8			1.5	
22/b		259 min	5280 4510	3510 2720	39.5 27.6 33.5			0.40	
22/a		168 h	23700	18260	1952				
22/b		168 h	22800 15400	17380	1781				
22/a		—	2520 3156	1551 2816	16.6 30.1 23.3				
22/b		—	3400	2618	26.8				The oxide layer polished off, and etched in taric acid solution

magnitude of the surface ion exchange will be about its four times. Nevertheless, our measurements showed the magnitude of ion exchange, referred to geometrical unit surface, to be almost identical. This phenomenon may be explained for by the fact that initial isotope exchange is governed by ion diffusion, which is identical for identical geometric conditions. On the other hand, with advancing time, surface areas, owing to etching by dissolution or to refinement by the dissolution of the peaks, tend to become of identical surface fineness, proportional to their geometry.

The rate determining role of ion diffusion is supported also by experimental results obtained in solutions of various concentrations. In general, investigations were carried out on 0.001 molar Fe(III) solutions, but also the exchange values measured on 0.1 molar solutions (Table 18) are identical. During the same unit time, a greater isotope exchange was found for solutions of higher temperature. (See e.g. in Table 19 experiments at 97 °C.)

Table XVI

Isotopic exchange in 0.001 molar FeCl$_3$ solution
Solution: 20 ml of 0.001 m Fe$_3$Cl + 1 ml of active FeCl$_3$
Activity of the solution: 4.96.10^6 c /100s; 3.00×10^{5}c/100s/ mg Fe

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)
23/a	2×3.99	1 min	1158 1108	680 645	5.7 5.4 5.6	0.47	16	0.35
23/b	2×3.8	1 min	1330 1188	900 700	7.9 6.2 7.1	2.7	90	0.08
23/a		6 min	2860 2820	1720 1700	14.4 14.2 14.3			0.9
23/b		6 min	3100 3000	1880 1820	16.7 16.1 16.4			0.18
23/a		18 min	3976 3564	2860 1750	23.8 14.6 19.2			1.2
23/b		18 min	4062 4054	2490 2480	22.0 22.0 22.0			0.25
23/a		35 min	5350 4925	3700 2530	30.9 21.1 26.0			1.6
23/b		35 min	6062 6152	3670 3740	32.5 33.0 32.7			0.36

Exchange investigations on stainless steel plates of type KORR-5 showed that no substantial isotope exchange took place even after 6 hours with 20 per cent of the surface atoms.

Our results indicate that further development of isotope exchange investigations will furnish a method suitable for the evalution of the corrosion behaviour of metals. In our further work, also the behaviour of activated steel plates in the solution of their own ions will be investigated.

Table XVII

Isotopic exchange in 0.2 molar HCl solution

Solution: 20 ml of 0.2 m HCl (inactive)

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Surface roughness measured (Ra, μm)	Rough-ness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)
23/a	(redissolving)	(initial activity)	5350 4925	3700 2530	30.9 21.1	26.0		
23/b	(redissolving)	(initial activity)	6062 6152	3670 3740	32.5 33.0	32.5		
23/a		1 min	5050 4256	3650 1756	30.5 14.7	22.7		
23/b		1 min	5408 5556	3080 3580	27.3 31.7	29.5		
23/a		6 min	3480 3518	2110 2140	17.6 17.8	17.7		
23/b		6 min	4036 4423	1980 3120	17.5 27.6	22.5		
23/a		20 min	2285 1465	1360		11.4		
23/a		20 min	2728 3198	1200 2480	10.6 21.9	16.2		
23/a			1760	1060	8.8	11.0		
23/b			1972 2121	970 1530	8.6 13.5			

Table XVIII

Isotopic exchange in 0.1 molar $FeCl_3$ solution
Solution: 20 ml of 0.1 m $FeCl_3$ + 1 ml of active $FeCl_3$
Activity of the solution: 4.42×10^6 c/100s; 51.50×10^4

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (c/100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)
24/a	2×2,0	10 min	223 192	167 122	16.2 11.8	0.64	21	0.77 0.56
24/b	2×2,38	10 min	404 348	340 219	27.8 17.9	2.7	90	0.31 0.20
24/a		35 min	720 660	560 400	54.4 38.8			2.6 1.85
24/b		35 min	1341 1224	1000 800	81.7 65.4			0.91 0.73
24/c	2×3,8	1 min	221 231	157	8.0	0.67	21	0.38
		13 min	1139 1211	750 905	42.4			2.0
		280 min	1427 1009	865	44.3			2.1
24/d	2×2,97	280 min	1139 855	940 442	61.6 28.9 45.3	0.64	21	2.15

Table XIX

Isotopic exchange in 0.001 molar $FeCl_3$ solution
Solution: 10 ml of 0.001 m $FeCl_3$ + 0.5 ml of active $FeCl_3$, at 97 °C
Activity of the solution: 2.24×10^6 c/100s; 2.39×10^5 c/100s/mg Fe

Plate No.	Geometrical surface (cm²)	Time exchange (test)	Activity measured (100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm²)	Remark
25	2×3,7	1 min	2079 1885	1570 1180	17.8 13.4	0.48	16	1.1	
		11 min	3363 3040	2520 1940	28.5 22.0			1.8 1.4	
		41 min	16000	11200	127.0				
			2319 1778	1940 1474	22.0 16.7			1.4 1.0	Slimy rust layer dissolved

Table XX

Isotopic exchange in 0.1 m $Fe(NH_4)_2(SO_4)_2$ solution

Solution: 20 ml of 0.1 m $Fe(NH_4)_2(SO_4)_2$ + 1 ml of active $FeCl_3$
Activity of the solution: 3.78×10^6 c/100s; 4.40×10^4 c/100s/mg Fe

Plate No.	Geometrical surface (cm^2)	Time exchange (test)	Activity measured (100s)	Activity calculated (c/100s)	Exchange referred to the geometric surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Surface roughness measured (Ra, μm)	Roughness factor calculated	Exchange to the actual surface ($x \cdot 10^{-4}$ mg Fe/cm^2)	Remark
26/a	2×4.83	1 min	411 439	274 316	12.9 14.8	0.48	16	0.8 0.9	
26/b	2×3.68	1 min	495 400	395 227	24.4 14.0 19.2	3.0	100	0.2	
26/a		19 min	890	630	29.7			1.8	
26/b		19 min	1273 1605	705 1290	43.5 79.8 61.6			0.6	
26/a		54 min	900	640	30.0			1.9	
26/b		54 min	1205 1305	800 955	49.5 59.1 54.3			0.54	
26/a		96.60 min	830 670	717 514	33.8 24.2			2.1 1.5	The „rust" pickled in tartaric acid solution
26/b		96.60 min	570 673	422 580	26.1 35.9			0.3 0.4	

Table XXI

Self-diffusion of metals

Metal	Mp., °C	Temp., °C	D cm^2/s	E kcal/g
α Fe	1555	800	3.1×10^{-13}	73.2
γ Fe	1520	1058	4.3×10^{-12}	74.2
Co	1495	1150	2×10^{-11}	67
Cu	1083	839	1.05×10^{-10}	47.15
Ag	960	936	4.6×10^{-9}	45.5
Hg	38.9	23	1.79×10^{-5}	1.16

Hevesy—Groh at 250 °C D_{Pb} 0.0001 cm^2/day

Summary

The isotopic exchange has been measured on pretreated (mechanical and short alkaline treatment) commercial low-alloy steel surfaces, in aqueous ferric chloride and Mohr's salt solutions, at room temperature, in function of time. The surface fineness of the plates used in the investigations has been determined experimentally, and from these values conclusions were drawn on the basis of proportionality of the magnitude of the actual surface. It was established that isotopic exchange without a change in the metal surface (structural transformations, corrosion, etc) takes place only over a certain percentage of the actual metal surface, and involves not more than a monomolecular surface layer. The exchange vs. time can be represented by the kinetic equation $\lg x = a \cdot \lg t + b$. Presumably, the rate determining process is the diffusion of iron ions in the solution.

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