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PROCESSES AND EQUIPMENT OF CHEMICAL INDUSTRY

Characteristics of the Reaction of Manganese Metal with Phenols, Alcohols, Water, and Their Mixtures with Each Other and with Carboxylic Acids in a Bead Mill

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Abstract—The macrokinetic relationships of the mechanochemical reaction of manganese with phenols, alcohols, water, and their mixtures with each other and with carboxylic acids taken in various molar ratios but, in some cases, in total stoichiometric amount were examined.

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Metal alcoholates and phenolates are widely used, in particular, for preparing high-purity oxides and oxide compounds, catalysts and adsorbents with highly developed surface [1], high-purity elements and oxide coatings [2, 3], for doping semiconductor compounds, for preparing specialty ceramics and thin and ultrathin coatings, and in nanotechnologies [4–6].

It is known [7] that only metals of Groups I and II vigorously react with alcohols and phenols. Under definite conditions, such reactions are also possible with metals of Group III. However, such reactions require catalysts and initiators whose role consists in overcoming the barrier caused by the presence of an impermeable oxide film on the metal surface. It is believed that metals of other groups of the periodic table cannot react with alcohols and phenols.

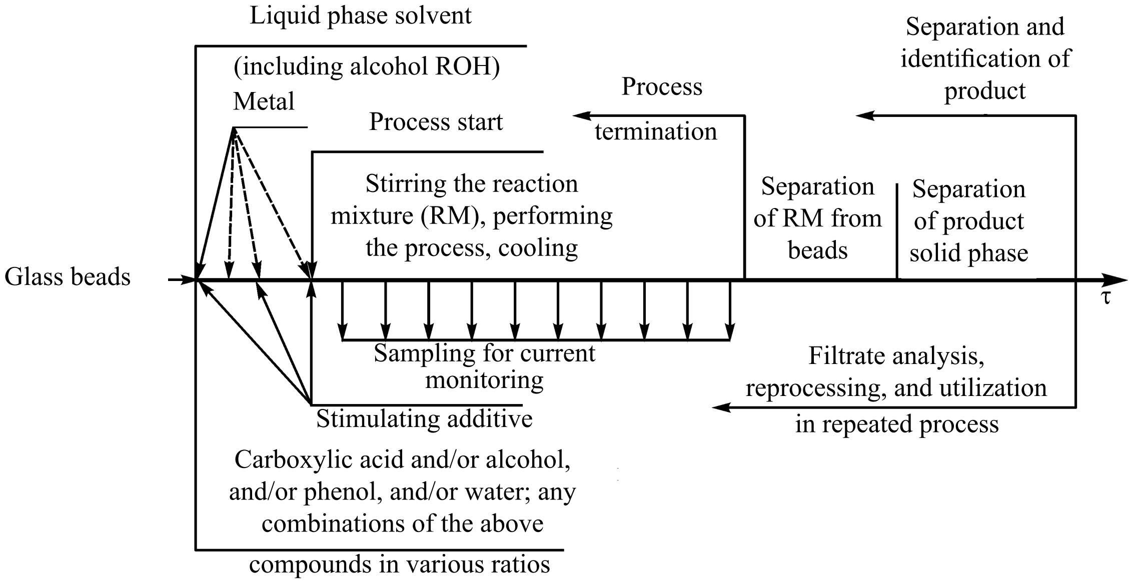
At the same time, under conditions of activation in a high-performance bead mill, it appeared possible to efficiently perform reactions of a number of heavy transition metals with many carboxylic acids [8–11] at technologically acceptable rates [12–20]. It was emphasized that the main problem in such processes is breakdown and removal of strong surface deposits of salts that are formed in the reaction and prevent the access of the acid to the reaction site, rather than breakdown of the oxide film initially present on the metal. Similar process seems to be feasible with alcohols and phenols. To check this assumption, we examined in this study the reactions of alcohols, phenols, and water with manganese in comparison with the reaction of manganese with oxalic acid.

EXPERIMENTAL

The experiment was performed in a vertical bead mill in accordance with the step-by-step scheme in which the horizontal line is the time axis (without consistent scale), arrows directed toward it denote feed streams, arrows denoted from the axis denote takeoff streams, and legends above and under the axis denote the main operations performed at the given instant of time.

In the above scheme, certain time can be provided for preparing reagent solutions in the chosen liquid phase solvent, and the moments of introducing the metal and stimulating additive can be varied. In some cases, this factor appeared to be significant. In current process monitoring, we primarily determined the content of Mn(II) compounds in the samples taken. In addition, we analyzed the residual amounts of the reagents taken in stoichiometric amounts or in deficiency, and also of manganese (in some cases). For this purpose, it was necessary to find such procedures of metal pretreatment

Step-by-step scheme of the process



before analysis with which the metal particles would be cleaned (at least partially) from surface deposits of the product. First and foremost, it was necessary to estimate the solubility of the products obtained in various media (Table 1).

As can be seen, in most cases the reaction products are poorly soluble in organic solvents. This fact explains why in the course of the reaction they are mainly accumulated in the solid suspended state, as reflected in the scheme.

The parameters of the reactor used are as follows. The casing is a cylindrical glass vessel with the inside diameter of 43, height of 121, and wall thickness of 2.5 mm. The vessel is covered with a thick plastic lid with a deep circular groove with a gasket on its bottom. The groove diameter corresponds to the vessel diameter. The stuffing box of the power-driven stirrer is arranged in the center of the lid, and on its side there are a pipe for connection with a reflux condenser and holes to arrange a sampler and a housing for measuring the reaction

Table 1. Estimation of the solubility of manganese oxalate, phenolate, and 2-methylpropan-1-olate in various solvents

Solvent	Solubility, mol kg^{-1}								
	oxalate (38.4% Mn)			phenolate (22.8% Mn)			2-methylpropan-1-olate (27.3% Mn)		
	at indicated temperature, °C, ±1								
	15	26	55	15	26	67	10	26	65
Ethyl acetate	0.020	0.017	0.015	0.022	0.004	0.007	0.016	0.018	0.020
Butyl acetate	0.017	0.031	0.009	0.036	0.007	0.011	0.016	0.032	0.020
DMF	0.017	0.036	0.009	0.029	0.010	0.018	0.028	0.035	0.052
2-Ethoxyethanol	0.018	0.017	0.007	0.027	0.010	0.017	0.017	0.021	0.013
1-Propanol	0.024	0.064	0.005	0.026	0.009	0.017	0.016	0.016	0.020
2-Propanol	0.022	0.024	0.009	0.078	0.009	0.012	0.015	0.022	0.021
1-Butanol	0.030	0.021	0.022	0.023	0.009	0.016	0.024	0.035	0.082
2-Methylpropan-1-ol	0.009	0.020	0.10	0.028	0.009	0.012	0.027	0.035	0.063
3-Methylbutan-1-ol	0.024	0.018	0.009	0.039	0.008	0.007	0.020	0.026	0.018
o-Xylene	0.021	0.039	0.008	0.015	0.010	0.016	0.014	0.018	0.018

mixture temperature. These holes are intermittently used for adding the required chemicals in the course of the process. The stirrer blade size is 41.5 × 40 × 3.7 mm. It is fixed in the slit of a textolite shaft of diameter 11 mm with two plastic pins. The stirrer shaft is connected to the driver shaft with a flexible connection. The driver power is 0.37 kW. The rotor rotation rate was 1560 rpm in most cases.

All parts of the installation are rigidly fixed on a special framework and have strictly fixed positions in all the steps of the work. The dismountable parts after the experiment completion were the cooling water bath in which the reactor casing was immersed to 0.5–0.8 of its height and the bead mill casing with the beads and reaction mixture. The bead size was 1.8–2.5 mm, and its weight ratio to the charge was (1.0–1.5) : 1.

Figure 1 shows the kinetic curves of the manganese consumption in its reactions with the acid, alcohol, phenol, and water taken separately. As can be seen, under the chosen conditions all these reactions start immediately and proceed to high conversions, with comparable reaction rates and times. It is important that the manganese conversion was practically quantitative

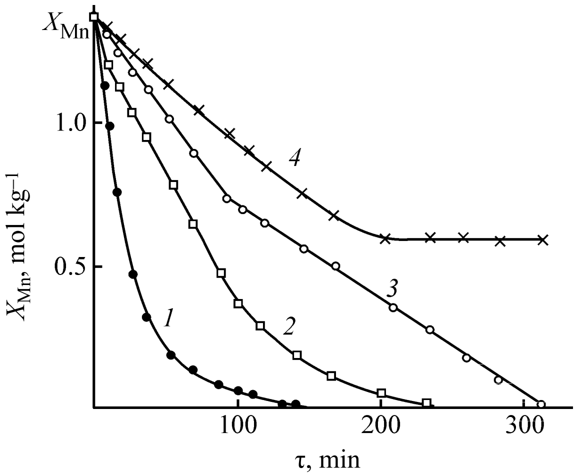


Fig. 1. Kinetic curves of manganese consumption in reaction with (*1*) oxalic acid, (*2*) 2-ethoxyethanol, (*3*) phenol, and (*4*) water. Reactor: vertical bead mill with textolite blade stirrer, gap between the blade and reactor casing 1.5 mm, beads to charge weight ratio 1.5 : 1, beads weight 120 g, temperature 33 ± 1°C. (X_{Mn}) Manganese content and (τ) time. Reactant ratio: (*1*, *3*) stoichiometric and (*2*, *4*) excess alcohol and water. Solvent: (*1*, *2*) 2-ethoxyethanol, (*3*) butyl acetate, and (*4*) water.

Table 2. Influence of the nature of alcohol as reagent and liquid phase solvent on the characteristics of its reaction with manganese metal in bead mill. Initial Mn content X_{Mn} = 1.4 mol kg^{-1}

Alcohol	Time, min, of attainment of indicated Mn conversion α				Reaction order[a]
	0.25	0.50	0.75	0.98 and above	
Methanol	50	100	150	200	Zero in the entire range of conversions
1-Propanol	42	84	145	300	Initially zero
2-Propanol	27	96	173	253	Initially close to zero, zero in the range α = 0.45–0.83
1-Butanol	87	175	280	418	Zero up to α = 0.85
2-Methyl-1-propanol	80	156	235	337	Initially close to zero
1-Pentanol	45	90	156	292	Zero up to α=0.55
3-Methyl-1-butanol	19	40	98	179	Initially close to zero
Cyclohexanol	67	138	237	388	"
1,2-Ethanediol	9	18	63	150	Zero
1,2-Ethanediol : butyl acetate = 1 : 1 (v/v)	14	27	43	79	"
2-Ethoxyethanol	40	80	100	120	Zero in the range α = 0.5–0.99

[a] The reaction order was determined as follows: by the coordinate transfer, we cut out a portion of the kinetic curve of the initial reagent consumption or product accumulation. Using known (in particular, integral) methods, this portion was checked for correspondence to one or another order; simultaneously, the boundaries of the cut-out portion were determined in the entire range of conversions of the reagent taken in deficiency.

Table 3. Influence of the nature of phenols on characteristics of their reaction with manganese metal in bead mill. Initial content, mol kg^{-1}: $X_{0_{\text{phenol}}} = 1.4$, $X_{0_{\text{Mn}}} = 0.7$; solvent butyl acetate, $T = 30 \pm 1$°C

Phenol	Time, min, of attainment of indicated Mn conversion α 0.98 and above				Characteristic of reaction mixture at high conversions
	0.25	0.50	0.75	0.98 and above	
Phenol	80	170	223	305	Moderately viscous suspension
o-Nitrophenol	31	63	94	148	Reaction mixture poorly separable from beads
m-Hydroxybenzaldehyde	10	35	80	150	Strong thickening at high conversions
p-Hydroxybenzaldehyde	63	160	260	320	Suspension, green filtrate
p-Cresol	50	100	150	215	Poorly separable suspension
2-Naphthol	100	220	280	340	Moderately viscous suspension

in its reaction with all the chosen alcohols and phenols (Tables 2, 3). Of course, the nature of the acid reagent plays an important role, determining the macrokinetic and time characteristics of the process and also the phase state of the reaction mixture and the dynamics of its variation in the course of the process. For different reagents, these characteristics are naturally different. Whereas alcohol was taken in a fairly large excess, because it simultaneously acted as a reagent and a solvent for the liquid phase, phenol was added in strictly stoichiometric amounts. These differences are partially associated with the fact that alcohols are weaker acids than phenols. However, nonchemical factors can also be important in the process. This indirectly follows from the presence of a certain optimum in the manganese content in the reaction mixture, at which the reaction rate is maximal and the process time is correspondingly minimal (Figs. 2, 3). With 2-propanol, which was

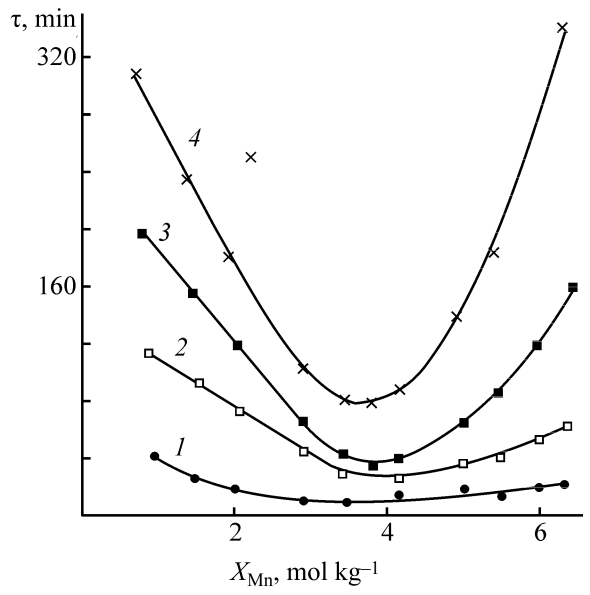


Fig. 2. Time τ_α of attainment of given conversion of manganese α in reaction with 2-propanol as a function of the initial Mn content X_{Mn}. Temperature 33 ± 1°C, no additional solvent, charge to beads weight ratio 1 : 1.4. Mn conversion α: (*1*) 0.25, (*2*) 0.50, (*3*) 0.75, and (*4*) 0.98 and above; the same for Fig. 3.

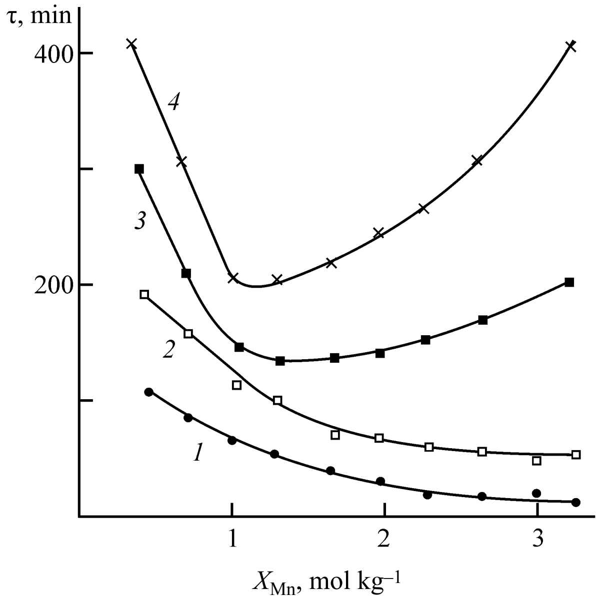


Fig. 3. Time τ_α of attainment of given conversion of manganese α in reaction with phenol as a function of the initial Mn content X_{Mn}. Stoichiometric ratio of metal and phenol, liquid phase solvent butyl acetate, temperature 33 ± 1°C, charge to beads weight ratio 1 : 1.25, stirrer rotation rate 1440 rpm.

chosen for systematic studies because with this alcohol, acting as both reagent and solvent, the reaction order changes from 1 to 0 (Table 2), such manganese content is 3.6–3.9 mol kg^{-1} (Fig. 2), and with phenol (the simplest representative of this class of acid reagents) it is somewhat greater than 1 mol kg^{-1}. Whereas with the alcohol the minimal time of attainment of any given degree of conversion is observed at the same initial content of the metal in the reaction mixture, with phenol the pattern is different: The lower the conversion, the more is the time minimum shifted toward higher initial manganese amounts.

It is impossible to attribute these phenomena to chemical interactions only. Most probably, they are associated with such factors as an increase in the content of abrasion products (fine metal particles), on the one hand, and thickening of the suspension by metal particles coated with surface deposits and by the product suspended in the liquid phase, on the other hand. As a result, the time required to attain any given degree of metal conversion as a function of the initial metal content passes through a minimum.

With water as reagent, the manganese conversion is quantitative very seldom, and usually it ranges from 40 to 85%. Then the process spontaneously decelerates, and it cannot be brought to completion within reasonable time. The process is additionally complicated by partial oxidation of $Mn(OH)_2$ with atmospheric oxygen (Fig. 4) whose contact with the reaction mixture was not specially limited. Probably, the presence of oxygen favors to certain extent more complete conversion of the metal.

As seen from Fig. 4, initially the major reaction product is manganese(II) hydroxide. With time, its accumulation stops. In the beginning of this period, compounds of manganese in a higher oxidation state are absent. The process cessation can be accounted for by full blocking of the metal surface with $Mn(OH)_2$ deposits. After accumulation of a definite amount of blocking deposits, oxidation of manganese(II) hydroxide with atmospheric oxygen occurred concurrently, and starting from a certain moment it led to partial opening of the metal surface and resumption of the formation of manganese(II) hydroxide, but at a considerably lower rate than in the initial moment, because the surface was opened only partially. Then, for a certain period, accumulation of Mn(II) and, apparently, Mn(IV) compounds occurs concurrently, following zero-order rate law. Then accumulation of Mn(II) compounds sharply ceases again, and after a certain period accumulation of manganese compounds in a higher oxidation state ceases also.

It cannot be excluded that this self-inhibiting process can resume again. In some cases this was indeed the case. However, this required, as a rule, longer time, and the resumed process ceased again. Presumably, surface deposits of products formed in the reaction of manganese with water are stronger and, hence, exert stronger hindering effect on the process than surface deposits of manganese carboxylates, alkoxides, and phenolates.

It was shown above that, under the chosen experimental conditions, manganese can react at comparable rates with acids, phenols, alcohols, and water, i.e., with reagents whose pK_a is in the range 2–18 and above. Clearly, pK_a is not a decisive factor in such processes. It was interesting to determine how the process characteristics would change on replacing a reagent by its mixture with another reagent so that the total amount of the reagents in the mixture would correspond to the stoichiometric ratio to the metal loaded. The results are given in Fig. 5 and in Tables 4–6.

As seen from Table 4, relatively small amounts of water in the charge, even if it is present in a certain stoichiometric excess, exert a moderate effect on the conversion and on the time in which the chosen degrees of metal conversion are attained. On the whole, the presence of water somewhat inhibits the combined redox

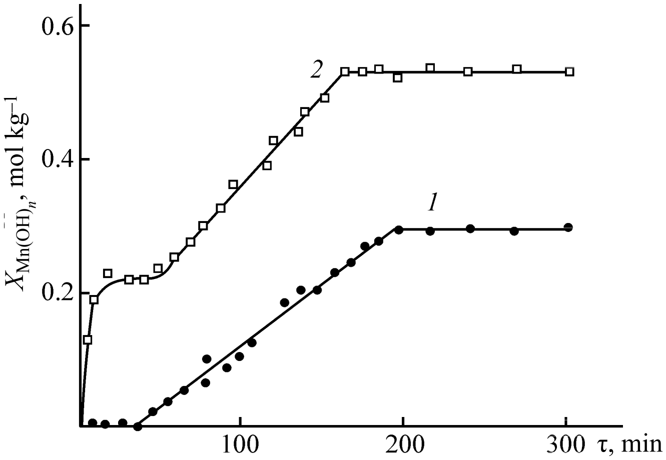


Fig. 4. Kinetic curves of accumulation of (*1*) manganese(II) hydroxide and (2) manganese(IV) hydroxide $X_{Mn(OH)_n}$ in the reaction of manganese with water under the conditions of curve *4* in Fig. 1. (τ) Reaction time.

process but does not alter many of its characteristics such as the presence of a minimum in the dependence of the time of practically complete metal conversion on the initial metal content (Fig. 5). Here it should be noted that such metal conversion often follows the rate equation for an irreversible zero-order reaction and that going to water as a solvent for the liquid phase and removal of glass beads from the reactor drastically deteriorate the process characteristics.

In the oxalic acid–2-ethoxyethanol reagent system, the times in which the given manganese conversions are attained as functions of the relative acid content pass through a minimum (Table 5). In other words, the addition of alcohol favors the reaction of the acid with the metal. This fact apparently explains why alcohols are among the most widely used solvents for liquid-phase processes for preparing carboxylates of manganese [12–14] and other metals [15–21].

Considerably more complex pattern is observed with the phenol–2-propanol and phenol–water systems (Table 6). With the components of these systems present in comparable amounts, the time in which the given degree of metal conversion is attained passes through a maximum. The time in this maximum considerably (sometimes by a factor of 5 and more) exceeds the process duration in the presence of only one component (but not water). It should be noted that, with water as the major component, small additions of phenol favor practically complete metal conversion at the highest rates for this system and within the shortest time. Similar pattern is observed with the phenol–2-propanol system, with the only difference that with the alcohol taken alone the process goes to completion without self-inhibition observed with water.

Presumably, these systems are characterized by the occurrence of a number of parallel heterogeneous

Table 4. Effect of the solvent and additive on the reaction of manganese with oxalic acid and water in bead mill at 30 ± 1°C. Weight ratio of charge to beads 1 : 1.25; initial content, mol kg^{-1}: $X_{\mathrm{Mn}} = 0.8$, $X_{\mathrm{ox.ac}} = 0.6$, $X_{\mathrm{H_2O}} = 1.2$

Liquid phase solvent	Additive, mol kg^{-1}	Time, min, of attainment of indicated Mn conversion α				Process characteristics
		0.25	0.50	0.75	0.98 and above	
Water	No additive	140[a]	No additive			Self-cessation on the 360th minute at α = 0.39
		10	23	44	78	$k = 0.026$ min^{-1}, $\alpha_{k = \mathrm{const}} = 0.73$
Water		10	20	38	60	$k = 0.020$ l mol^{-1} min^{-1}, $\alpha_{k = \mathrm{const}} = 0.53$
p-Xylene		28	41	65	110	Pronounced self-acceleration period at the beginning
White spirit[b]		12	24	43	71	Order close to zero up to α = 0.5
White spirit		15	39	80	128	$k = 0.020$ min^{-1}, $\alpha_{k = \mathrm{const}} = 0.48$
Butyl acetate		24	56	88	120	Order close to zero in the range α = 0.15–0.95
1-Propanol		12	37	61	132	No range with clear reaction order
1-Butanol		7	16	40	80	Order close to zero from α = 0.61
2-Ethoxyethanol		6	20	45	80	No range with clear reaction order
1-Butanol	Water, 1.53	8	24	70	150	Order close to zero after α = 0.61
	NaCl, 0.06	10	24	71	121	Intermediate self-inhibition followed by self-acceleration at α = 0.75
	KI, 0.06	20	78	143	220	Zero order after α = 0.30
	NH_4Cl, 0.06	13	35	110	180	Zero order after α = 0.50
	I_2, 0.06	9	18	46	84	Zero order up to α = 0.50, $k = 0.022$ l mol^{-1} min^{-1}

[a] Without glass beads.

[b] Fraction boiling out up to 180°C.

Table 5. Influence of the stoichiometric deficiency of oxalic acid on its reaction with manganese in 2-ethoxyethanol in a bead mill at 25 ± 1°C

Oxalic acid dosage, % of stoichiometric amount значения	Time, min, of attainment of indicated Mn conversion α				
	0.10	0.25	0.50	0.75	0.98 and above
100	3	8	18	37	113
95	2	5	15	31	87
90	1	3	13	25	75
85	2	5	15	30	83
80	3	8	19	40	119
70	4	12	37	68	130
60	5	13	38	68	145
50	7	14	36	62	161
40	7	13	35	55	158
30	7	13	33	49	152
20	8	14	31	46	150
15	8	14	31	48	150
10	8	14	31	50	155
5	9	15	37	70	163
0	11	40	65	125	238

reactions involving the metal and consecutive-parallel reactions involving primary transformation products, e.g., basic salt. However, it is difficult and even hardly possible to attribute the observed maxima to this factor. Most probably, the cause is associated with different strengths and structures of the blocking deposits formed on the metal surface. The composition of these deposits is naturally variable, so that in the course of the reaction their strength can both increase and decrease. Numerous examples can be found in the literature [9]. The use of various stimulating additives is also associated with this phenomenon.

It was already noted above that, in some cases, the product accumulation occurred in accordance with the rate equation for an irreversible zero- and/or first-order reaction. Because the processes are heterogeneous and diffusion-controlled and the reaction rate on replacement of only a liquid phase solvent can change by a factor of not only several units, but even several tens and hundreds, there are no grounds to search for chemical schemes to account for the observed fact. It seems more probable that the process is controlled by the step of transport of the reagent Re occurring in the liquid phase to the site of the chemical reaction via adsorption. The process is described by the main mass transfer equation

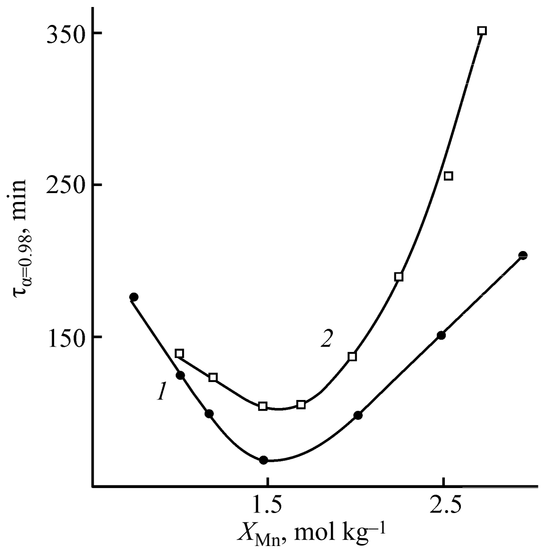


Fig. 5. Time of attainment of practically quantitative conversion of Mn metal to Mn(II) compounds in the reaction of manganese with oxalic acid (71.4% of stoichiometric amount) and water introduced with the acid (water of crystallization), $\tau_{\alpha=0.98}$, as a function of the initial Mn content X_{Mn}. Liquid phase solvent 2-ethoxyethanol, temperature 29 ± 1°C. (*1*) Without additives and (*2*) in the presence of 0.4 mol kg^{-1} MnO_2 and 0.05 mol kg^{-1} iodine.

$$W = K_R F_R([\mathrm{Re}] - [\mathrm{Re}]^*), \qquad (1)$$

where K_R and F_R are, respectively, the mass transfer coefficient (adsorption coefficient of reagent Re) and working (not occupied by product deposits) area of the phase contact surface; [Re] and [Re]* are the running and equilibrium (with the surface concentration on the metal) concentrations of the reagent whose adsorption on the metal surface is the limiting step of the process.

If the chemical reaction on the surface is fast, the surface concentration of the reagent Re will tend to zero. Hence, $[\mathrm{Re}]^* \to 0$ and

$$W = K_R F_R[\mathrm{Re}]. \qquad (2)$$

Here the result will largely depend on the type of the function $F_R = f(\tau)$. If $F_R \approx$ const, which is quite realistic when the major part of the physical surface area is

Table 6. Influence of the molar ratio of phenol to 2-propanol or water in the initial solution on the reaction of these agents with manganese at 22 ± 1°C in butyl acetate as liquid phase solvent in bead mill. Initial Mn content 1.0 mol kg^{-1}

Reagent, mol kg^{-1}		Time, min, of attainment of indicated Mn conversion α				
phenol	2-propanol (water)	0.10	0.25	0.50	0.75	0.98 and above
Phenol–2-propanol						
2.00	0	10	60	92	118	150
1.97	0.03	23	132	233	342	684
1.90	0.10	125	480	705	970	1560
1.75	0.25	120	354	531	745	1270
1.50	0.50	103	251	383	482	811
1.25	0.75	43	120	210	285	410
1.00	1.00	57	95	154	200	288
0.75	1.25	49	88	157	211	282
0.50	1.50	40	82	161	238	287
0.25	1.75	8	61	93	120	150
0.10	1.90	7	33	87	145	165
0	2.0	19	57	121	214	321
Phenol–water						
1.95	0.05	25	60	113	163	219
1.80	0.20	75	108	138	158	175
1.65	0.35	55	108	215	320	480
1.50	0.50	38	105	275	480	570
1.25	0.75	33	112	253	407	550
1.00	1.00	25	118	192	350	540
0.75	1.25	21	106	173	307	458
0.50	1.50	13	63	158	263	337
0.25	1.75	16	36	65	94	125
0.15	1.85	57	80	92	113	150
0.05	1.95	41	115	197	243	479
0	2.00	33	127	572	Not attained in 1250 min	

blocked by product deposits (F_B), i.e., when $F_R << F_B$, then at $K_R \approx$ const Eq. (2) will take the form of a rate equation for an irreversible first-order reaction:

$$W = k_{\text{eff}}[\text{Re}]. \tag{3}$$

At a large excess of reagent Re, e.g., when an alcohol is used both as reagent and as liquid phase solvent, the rate equation of the reaction will take the form of a zero-order rate equation:

$$W = \text{const}. \tag{4}$$

The correspondence to Eq. (3) or (4) is possible only in certain (sometimes large with respect to conversion intervals) steps of the process. There is always a moment when Eqs. (3) and (4) cease to be observed. Furthermore, there may be cases when the reaction does not clearly follow Eq. (3) or (4) at all. At a large excess of the reagent, the reaction instead of Eq. (4) can follow Eq. (3) or a certain, more complex, equation.

This depends on the form of the function $F_R = f(\tau)$, determined by the parameters of the steps of breakdown of surface deposits and fine disintegration of particles changing their size owing to surface deposits. If there were no surface deposition, the metal particle size would not increase in the course of the process. Only disintegration to the size determined by the performance of the bead mill would be observed. On reaching this moment, the process would sharply decelerate up to practical cessation. Virtually 100% metal conversion into the product would never be attained. In practice, however, it is attained, and rather frequently. Here we can see the positive role of the surface deposits.

CONCLUSIONS

(1) In an efficiently operating bead mill, manganese metal fairly readily, rapidly, and in many cases quantitatively reacts not only with carboxylic acids, but also with fatty alcohols, phenols, water, and mixtures of these compounds in the form of their solutions in organic solvents. Despite very large difference in pK_a values for acids, phenols, and alcohols, the rates of the reaction of these compounds with manganese are not only comparable but often even close.

(2) Oxidation of manganese with water leads to the formation of comparable amounts of Mn(II) compounds and compounds of Mn in a higher oxidation state, formed by heterogeneous oxidation of Mn(II) with atmospheric oxygen.

(3) In reactions of manganese with mixtures of acidic reagents, both significant acceleration and strong deceleration of the overall redox process can be observed, depending on the molar ratio of the acidic reagents, their nature, and absolute amount of each reagent in the reaction mixture.

(4) The observed correspondence of the kinetic curves for separate components of the system to rate equations for irreversible zero- and first-order reactions is accounted for by the mechanism in which the limiting step is adsorption of the reagent dissolved in the liquid phase on the working surface of manganese as the site of the redox reaction.

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