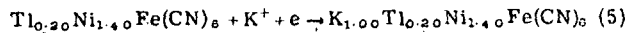To regenerate the oxidised electron ion exchanger (sample C) we used its reduction in the presence of K^+ ions:

$$Tl_{0.20}Ni_{1.40}Fe(CN)_6 + K^+ + e \rightarrow K_{1.00}Tl_{0.20}Ni_{1.40}Fe(CN)_6 \quad (5)$$

As reducing agent we used a 0.093N solution of ascorbic acid. The amount of the potassium salt in the solution represented a fourfold excess over the stoichiometric amount according to equation (3). The dependence of φ on m_{red}, where m_{red} is the amount of reducing agent consumed [mg-eq/mg-mole $Fe(CN)_6$], is shown in fig. 1. As seen, complete reduction of Fe(III) to Fe(II) occurs in the ferrocyanide. The potential φ at the endpoint of the reduction amounts to 0.57V. According to this potential, solutions of K^+, $S_2O_3^{2-}$, $K^+ + SO_3^{2-}$, and others can be used as reducing agents. The amount of K^+ ions entering into the composition of the electron ion exchanger during the reduction x, [mg-eq K^+/mg-mole $Fe(CN)_6$] corresponds strictly to the fraction of reduced $Fe(CN)_6$ groups (fig. 3). The reduction results in the formation of a ferrocyanide with the composition $K_{1.00}Tl_{0.20}Ni_{1.40}Fe(CN)_6$, which is ready for the next cycle of sorption of Tl^+ ions.

Conclusions

The desorption of thallium from the mixed nickel thallium ferrocyanide can be realised by oxidation the ferrocyanide to ferricyanide. The sorbent can be regenerated by reduction.

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The mechanism and kinetics of the hydrolytic precipitation of Fe(III) from zinc sulphate solution

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The hydrolytic precipitation of iron plays a deciding role in the leaching of zinc calcines. However, there are no reliable data on its mechanism, and its kinetics have been insufficiently investigated. Data on the phases precipitated from solutions in the $Fe_2O_3 - SO_3 - H_2O$ system[1][2] cannot be transferred a priori to zinc solutions. Indications of the formation of basic sulphates and iron hydroxide during hydrolysis of iron in the hydrometallurgy of zinc are non-specific[3], since a series of compounds are formed. In[4-9] almost all the known solid products from the hydrolysis of $Fe_2(SO_4)_3$ were synthesized and their individualities were confirmed by IR spectroscopy and thermal analysis, but only a few of them are formed during the precipitation of Fe(III) from sulphate solutions with alkalis[9-11]: Jarosite $(R, H_3O) Fe_3(OH)_6 (SO_4)_2$ and the amorphous basic sulphate $2Fe_2O_3 \cdot SO_3 \cdot xH_2O$ as primary precipitation products, and goethite α-FeOOH as secondary product.

The purpose of the present work was to study the mechanism and kinetics of the hydrolytic precipitation of iron in the $Fe_2(SO_4)_3 - ZnSO_4 - ZnO-H_2O$ system at 50-90°C under various concentration conditions (initial concentrations $C_{0\ Fe} = 0.05-15$ and $C_{0\ Zn} = 0$ and 100 g/l).

Table 1: The phase composition of the precipitates as a function of the temperature, the molar ratio $m = ZnO/Fe_2(SO_4)_3$, and time with initial $C_{0\ Fe} = 12$ g/l and $pH_0 = 1.2$ in the $Fe_2(SO_4)_3 - ZnSO_4 - ZnO-H_2O$ system, where $C_{0\ Zn} = 100$ g/l

t, °C	m	Phase composition of precipitates (holding time, h)
90	1.0	A/G/(0.5); G(2-24)
	2.0-3.0	A(1/12); G(2-24)
	3.5	A/G/(2)
70	1.0	A(2); A/G/(7); G(24-120)
	2.0	A, G(1/12); G/A/(7); G(24-120)
	3.0	G(2-120)

Note: A = amorphous basic sulphate; G = goethite. Semi-quantitative ratios of the phases: A, G-phase G less than phase A; A/G/- phase A is the main phase, and phase G the impurity phase.
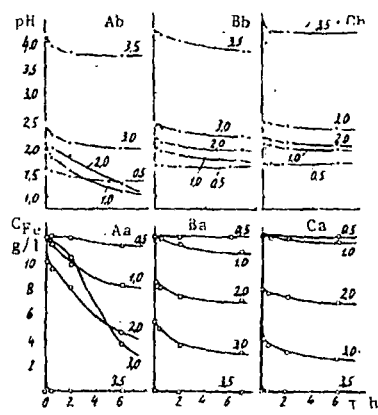

Fig.1
The variation of the concentration of iron (g/l, a) and pH (b) in solutions of the $Fe_2(SO_4)_3-ZnSO_4-ZnO-H_2O$ system with time (h) at 90 (A), 70 (B), and 50 (C) °C. C_0 Zn = 100 g/l. The numbers of the curves correspond to the values of the molar ratios $m = ZnO/Fe_2(SO_4)_3$.
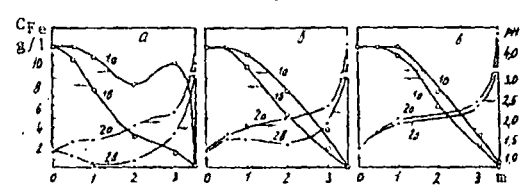

Fig.2 The concentrations of iron (g/l, 1) and the pH values (2) in solutions of the $Fe_2(SO_4)_3-ZnSO_4-ZnO-H_2O$ system as a function of m at 90 (a), 70 (b), and 50 (c) °C. C_0 Zn = 100 g/l. Curves 1 and 2 with letters a and b relate to holding times of 2 and 24 h respectively.
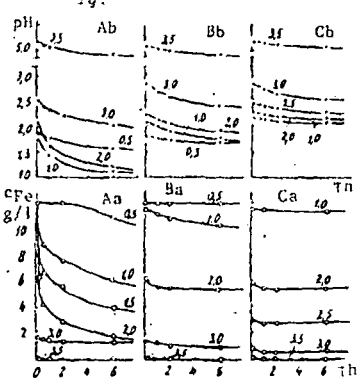

Fig.3
The variation of C_{Fe} (g/l, a) and (b) in solutions of the $Fe_2(SO_4)_3-ZnO-H_2O$ system with time at 90 (A), 70 (B), and 50 (C) °C.

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The procedure was similar to that described in[9]. The kinetics of the hydrolytic precipitation of Fe(III) are characterised by data on the variation of the pH and c_{Fe} with time (e.g., for c_0 $_{Fe}$ = 12 g/l in figs.1-3). The phase composition of the precipitates (table 1), established by IR spectroscopy, characterises the mechanism of the process. We note that the semi-quantitative estimates of the contents of the phases are relative, i.e., they only indicate an increase or decrease in the amounts of the given phase in relation to the others. For example, the secondary crystalline phase can be masked by the primary amorphous phase. The data in table 2 characterise the phase transitions in the precipitates.

Table 1: The degree of conversion (α, %) of the amorphous basic sulphates to goethite at 90°C as a function of the conditions

Conditions	Time, h	α, %	pH
Aqueous solution of NaOH, pH_0 = 4.5; solid:liquid 1:100	1	5.8	4.21
	3	8.0	3.72
	24	18.3	2.64
	120	68.2	-
Aqueous suspension of ZnO in stoichiometric amount, solid:liquid = 1:4	12	5.4	6.15
	2	22	6.05
	6	24.3	6.10
	24	32	6.05

The reasons for the observed changes in c_{Fe} and pH with time can be explained on the basis of theories about the mechanism of the hydrolytic precipitation of Fe(III)[12][13]. The addition of ZnO converted to $Zn(OH)_2$ to the solution gives rise to partial neutralisation of the acid (a sharp rise of pH from 1.2 to 1.5-4.4, as seen from fig.1) and rapid exchange hydrolytic transformations of the aqua, hydroxo, and sulpho complexes of Fe(III) to more basic complexes with the conversion of $Zn(OH)_2$ into $ZnSO_4$. The initial rise of ΔpH_{in} shifts the hydrolysis state of Fe(III) in the solution from the equilibrium value and stimulates the hydrolysis reaction itself of the iron ions (slow decrease of pH, see figs.1 and 2).

Increase in the pH and the concentration of the hydroxo complexes of Fe(III) in the solution assists the formation of polynuclear complexes of iron, and as a result of the tendency of the latter to oxidise their polymerisation of the polycondensation type develops with the formation of colloidally disperse particles. Further consolidation of these particles leads to the formation of the amorphous hydrated oxosulphate $2Fe_2O_3 \cdot SO_3 \cdot xH_2O$[9]. The indicated composition of this compound was established in[9] during its precipitation from a dilute solution of $Fe_2(SO_4)_3$. It is not impossible that during the precipitation from solutions more concentrated in SO_4^{2-} the basic sulphate acquires a variable composition, which changes towards a decrease in the basicity of the compound. However, it is difficult to establish this on account of the absence of reliable methods for determination or calculation of the amount of solution trapped by the amorphous precipitate without destroying the composition of the latter.

The amorphous basic sulphate is the primary product from the hydrolytic precipitation of Fe(III) from zinc sulphate solutions and changes into goethite with time (table 1). This phase transition is observed over the whole investigated range of Fe(III) concentrations in the solution and is accelerated with increase of the pH and temperature (table 1), but this transition takes place fairly slowly even at the initial pH_0 = 4.5 at 90°C, is retarded with time, and is accompanied by a decrease in the pH value (table 2), which is due to release of acid during the reaction.

$$2Fe_2O_3 \cdot SO_3 \cdot xH_2O = 4FeOOH + H_2SO_4 + (x - 3) H_2O \quad (1)$$
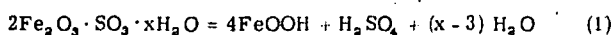
The retardation of the transformation with time is due not to the accumulation of acid in the solution but to diffusion retardation of the removal of the acid into the solution, which is created by the goethite crust on the particles of amorphous sulphate. This can be seen from the fact that the rate of reaction[1] decreases considerably at a relatively small degree of conversion of the initial compound even with a high and practically constant pH value of 6 (table 2, neutraliser ZnO).

The secondary character of the α-FeOOH is due to the fact that the polycondensation of the hydroxo complexes of iron (III) which rapidly develops in the solution, leading to the formation of the amorphous precipitate, excludes the formation of centres for the crystallisation of goethite in the solution. As a more stable phase, the goethite is therefore formed during ageing of the amorphous precipitate of basic sulphate on account of the occurrence of reaction[1]. The mechanism of this transition was described in[14].

It was established that with a concentration c_{Fe} > 0.1 g/l the initial product from precipitation of Fe(III) is the amorphous basic sulphate, while when c_{Fe} ≤ 0.1 it is the amorphous hydrated iron(III) oxide[9], which also changes into goethite during ageing.

On the basis of the data obtained in the work it is possible to make the following judgements about the kinetics of the process.

From the variation of the pH of the solutions with time it is seen (figs.1 and 2) that in the $Fe_2(SO_4)_3$-$ZnSO_4$-ZnO-H_2O system the hydrolysis rate of Fe(III) decreases with decrease of c_{Fe} and of the initial shift of ΔpH_{in} in the solution. For example (fig.1, at 90°C with a small ΔpH_{in} (specific consumption of neutraliser m = $ZnO/Fe_2(SO_4)_3$ = 0.5 the hydrolysis rate is low with a high value for c_{Fe}. With increase in m, ΔpH_{in} increases, but c_{Fe} decreases (on account of exchange reactions). The hydrolysis rate passes through a maximum with increase in m but decreases regularly with time on account of decrease in c_{Fe} and of the accumulation of hydrolysis acid, i.e., approach to hydrolysis equilibrium in the solution. We note the slow decrease of the pH value with time under the conditions of practically complete precipitation of iron (e.g., see fig.1 Ab, curve 3.5 or fig.2, curves 2a, c for m = 3.5), which is due to the occurrence of reaction[1].

With other conditions equal the ΔpH_{in} value, which plays an important role in the kinetics of the process, increases with decrease in temperature (fig.1), and this is explained by the superimposition of three processes, i.e., neutralisation of the acid in the solution, exchange hydrolytic reactions, and the true hydrolysis reactions of iron. The first two processes are practically independent of temperature, but the hydrolysis of iron (it reduces the ΔpH_{in} value) is retarded with decrease in temperature (figs.1 Ab, Bb, Cb), and the contribution from hydrolysis to ΔpH_{in} increases with increase in the initial neutralisation of the acid, i.e., with increase in the departure from hydrolysis equilibrium. On account of this, ΔpH_{in} increases with decrease in temperature and the more so, the greater the m value.

The kinetics of the precipitation of iron have two clearly defined stages, i.e., rapid precipitation in the initial period and then slow precipitation. The rapid precipitation results from the sharp increase in the concentration of the hydroxo complexes on account of exchange reactions with the $Zn(OH)_2$ base and their rapid oxidation with the formation of a precipitate of amorphous basic sulphate. When the sharp initial supersaturation of the solution by the hydroxo complexes is removed by the passage of the iron into the precipitate, the subsequent formation of the precipitate is retarded and is maintained by the formation of hydroxo complexes on account of the true hydrolysis reactions. If the initial rise ΔpH_{in} is small, the formation rate of the precipitate depends on the hydrolysis rate, and there is an induction period for the formation of the precipitate of amorphous basic sulphate (fig.1 Aa and 1 Ba, curves 0.5).

The rate of precipitation of the iron is affected by ΔpH_{in}, c_{Fe}, and C_{ZnSO_4} and also by temperature. The presence of considerable amounts of $ZnSO_4$ in the solution substantially distorts the effect of the other factors on the iron precipitation rate. It is therefore expedient to compare the kinetics of the process for c_0 $_{Zn}$ = 100 g/l (fig.1) and c_0 $_{Zn}$ = 0 (fig.3).

From fig.3 it is seen that the precipitation rate of Fe(III) in the fast stage is proportional to the initial shift ΔpH_{in}

with other conditions equal (compare the curves for the various m values in fig.3 Aa or 3 Ba or 3 Ca), while, at the stage of slow precipitation it is proportional to the rate of the true hydrolysis of Fe(I) and consequently (like the hydrolysis rate) varies extremal with increase in m, i.e., the consumption of the neutraliser. Decrease in temperature reduces the precipitation rate at the stage of slow precipitation, and at the stage of fast precipitation it retards it for small m values and hardly changes it at all for large m values. (The latter probably results from compensation for the decrease in the temperature factor by the increase in the concentration factor, i.e., ΔpH_{in}).

With other conditions equal (figs.1 and 3) the content of $ZnSO_4$ in the solution reduces ΔpH_{in} (particularly with a large consumption of ZnO, e.g., for m = 3.5, which is due to partial consumption of the ZnO neutraliser on hydrolytic reaction with $ZnSO_4$[16]) instead of neutralisation of the acid), retards the hydrolysis of Fe(III) (due to the buffer action of $ZnSO_4$)[16]), and retards the precipitation of iron. The precipitation rate of Fe(III) at the fast precipitation stage decreases with increase in temperature (figs.1 Aa, Ba, and Ca), and at $90^{o}C$ this stage only appears when $m \geqslant 3.5$. The retardation of the precipitation of Fe(III) becomes stronger with increase in the $ZnSO_4$ content of the solution; after 24h with m = 2 for $c_{0\,Fe} = 5\,g/l$ the increasing $c_{0\,Zn}$ values of 0, 50, and 150 g/l correspond to Δc_{Fe} values of 3.49, 2.94, and 2.32 g/l respectively, and for $c_{0\,Fe} = 12\,g/l$ the increasing $c_{0\,Zn}$ values of 0 and 100 g/l correspond to Δc_{Fe} values of 9.00 and 6.88 g/l.

The retarding effect of $ZnSO_4$ on the hydrolytic precipitation of Fe(III) becomes stronger with increase in temperature and is explained by the stabilising action of the electrolyte ($ZnSO_4$) on the colloidally disperse state of Fe(III) in the solution. At $90^{o}C$ with $z_{0\,Zn} = 100\,g/l$ and $c_{Fe} \geqslant 7.5\,g/l$ in the pH region of 2 - 3.5 this converts the iron to the state of a hydrogel, which represents a transparent red-brown viscous solution (a structured liquid). Here the formation of the precipitate (coagel) of the amorphous basic sulphate is greatly retarded; when m = 3, the precipitation rate of Fe(III) is considerably lower than with small values of m (fig.1 Aa, curve 3.0, or fig.2a, curve 1a). This retardation of the passage of Fe(III) into the precipitate becomes stronger with increase of c_{Fe} in the solution (fig.4). The sharp increase of the light scattering (by several times) in high-iron zinc solutions at pH 2 - 3.5 compared with pure-iron solutions with equal c_{Fe} values confirms that the Fe(III) is converted into the state of a hydrogel in the zinc solutions.

Fig.4
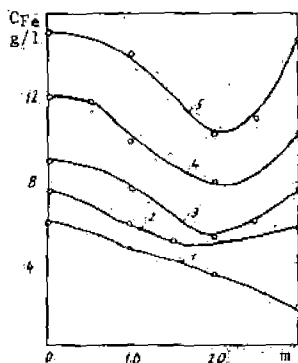The c_{Fe} values (g/l) after holding for 2h in solutions of the $Fe_2(SO_4)_3$-$ZnSO_4$-ZnO-H_2O system as a function of m at $90^{o}C$ with various $c_{0\,Fe}$ values, g/l; 1 - 6; 2 - 7.5; 3 - 9; 4 - 12; 5 - 15. $c_{0\,Zn} = 100\,g/l$.

The obtained results reveal the character of the effect of various factors on the composition and state of the hydrolytic precipitates of iron and on the rate of hydrolytic precipitation of Fe(III) from zinc sulphate solutions, and this is essential as preliminary information for the construction of a mathematical model and in the search for optimum process conditions.

Conclusions

1. The primary products from hydrolytic precipitation of Fe(III) from zinc sulphate solutions are an amorphous basic sulphate $2Fe_2O_3 \cdot SO_3 \cdot xH_2O$ when $c_{Fe} \geqslant 0.1\,g/l$ and an amorphous hydrated iron oxide when $c_{Fe} \leqslant 0.1\,g/l$. With time the amorphous phases change into crystalline goethite α-FeOOH with retardation.

2. The hydrolytic precipitation of Fe(III) takes place in two stages, i.e., a fast and then a slow stage. The precipitation rate (v_{Fe}) increases with increase in the initial neutralisation of the solution ($pH_0 = 1.5 - 5.2$) and with increase in the concentration of iron in the solution ($c_{Fe} \leqslant g/l$) during the fast precipitation stage; during the slow precipitation stage v_{Fe} depends extremal on the initial neutralisation of the solution (passes through a maximum). With increase in the $ZnSO_4$ content of the solution ($c_{0\,Zn} = 0$-150 g/l) v_{Fe} decreases. With increase in temperature (50-$90^{o}C$) v_{Fe} decreases in the fast precipitation stage and increases slightly in the slow precipitation stage (as a result of intensification of the retarding action of $ZnSO_4$ with increase in temperature).

3. For a high-iron ($c_{Fe} > 7g/l$) zinc sulphate solution with pH 2-3.5 a rise in temperature to $90^{o}C$ is risky, since it leads to the formation of a viscous hydrogel of iron, which greatly retards the formation of the hydrolytic precipitate. Increase in c_{Fe} stabilises the hydrogel.

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Determination of the accuracy and improvement of the method for determination of the diffusion coefficient by means of capillaries in the solid-liquid system

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Summary

A new method was developed for the determination of the position of the boundary between the solid and liquid phases in the capillary. The method extends the possibilities for the use of capillary models during investigation of diffusion