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SORPTION PROPERTIES OF IRON(II) SULPHIDE PREPARED BY THE SOL–GEL METHOD

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SUMMARY

A novel method for the preparation of inorganic ion exchangers based on insoluble iron(II) sulphide, their characteristics and their application to the recovery of some heavy metals from dilute solutions are described.

INTRODUCTION

Less soluble sulphides, marked by the selective uptake of some heavy metal ions, are important inorganic ion exchangers. The literature dealing with the exchange properties of natural and synthetic sulphides is summarized in detail in refs. 1–3. The formation of sulphides and their properties (mainly their solubilities) have been thoroughly studied as a result of the application of the hydrogen sulphide system in analytical chemistry over many years. Sulphides can be arranged in order of decreasing solubilities, which determine their relative reactivity[4,5]: $MnS > FeS > ZnS > NiS > CoS > PbS > CdS > Bi_2S_3 > CuS > Ag_2S > HgS$. Each element can be displaced from the solid phase into solution by the ions of an element that forms a less soluble sulphide[5]. This fact has been utilized for the selective precipitation of some elements on cadmium and zinc sulphides[6].

The synthetic sulphide ion exchangers used so far have usually been prepared by classical precipitation reactions. In many instances, however, the products thus obtained exhibit too poor mechanical properties for use in chromatographic columns. The mechanical properties of precipitates have been improved by the application of various inert supports[2] or by freezing-out[7,8]. However, they still do not match the common properties of ion-exchanger resins, especially as regards regularity of particle shape and mechanical stability.

Better properties can be attained by applying the sol–gel process, for which it is characteristic that the product (a hydroxidic hydrogel) is obtained in the form of regular firm beads. From hydrogels, the corresponding sulphides can be prepared by replacement of the hydroxyl groups[9]. The original spherical particle shape is not changed during the conversion.

Of the elements that readily form both hydrogels and less-soluble sulphides, iron should be mentioned first. The relatively high instability of iron(II) sulphide towards oxidation is a drawback but, on the other hand, its position in the solubility series is favourable. From the practical point of view, its main advantages lie in the low price of iron salts and in the fact that iron ions are biologically harmless, which is not so for any of the elements that have so far been used as the sulphides for chromatographic purposes. The position of iron(II) sulphide in the solubility series suggests that this compound, prepared in a suitable way, could be useful for the sorption of some important chalcogenic elements from dilute solutions. Mellor[10] presented several examples of the precipitation of such elements from solutions of their salts by the action of iron(II) sulphide. These are the main reasons that induced us to study the conditions for the preparation of spherical iron(II) sulphide and its sorption properties.

EXPERIMENTAL

Chemicals

Sodium sulphide (p.a. grade, Lachema, Brno, Czechoslovakia) solutions with an $Na^+:S^{2-}$ ratio of 2.10 were used. Ammonium sulphide (p.a. grade, Lachema) was used in the form of an aqueous solution, in which the concentrations of NH_4^+ and S^{2-} ions were 13.4 and 2.68 M, respectively. A solution of sodium hydrogen sulphide was prepared by saturating a solution of the normal salt with gaseous hydrogen sulphide; the concentrations of Na^+ and S^{2-} ions in the initial solution were determined to be 1.72 and 1.61 M, respectively. Gaseous hydrogen sulphide was evolved in the usual way by decomposing iron(II) sulphide with hydrochloric acid. The other chemicals used were of p.a. purity.

For the preparation of the emulsion, SPAN-80 (Koch-Light, Colnbrook, Great Britain) was used. The radioactive nuclides ^{203}Hg, ^{110m}Ag, ^{75}Se, ^{124}Sb, ^{46}Sc, ^{65}Zn and ^{60}Co were prepared by irradiation in a reactor and were used in concentrations of less than 10^{-5} mole $\cdot l^{-1}$.

The iron content in individual samples was determined gravimetrically as Fe_2O_3 and the concentration of Fe^{2+} ions in the eluate was determined by manganometric microtitration[11]. The overall sulphur content was determined after preliminary oxidation as barium sulphate[12]. The sulphide-sulphur was determined by decomposition in an acidic medium, absorption of the hydrogen sulphide in cadmium sulphate solution and iodimetric titration[11].

The concentrations of the radionuclides before and after sorption were determined by gamma-ray spectrometry. The measurements were performed by using a Ge(Li) detector with a volume of 32 ml (F.W.H.M. resolution, 2.6 keV for 1332.4-keV ^{60}Co; peak to Compton ratio, 20:1), connected through a pre-amplifier and an amplifier to a 4096-channel analogue-to-digital converter (100 MHz) which was interfaced to the small computer Multi-8 (24 K) of the Plurimat-20 system (Intertechnique).

Procedures

The iron(III) hydroxide conversion was studied under static conditions by stirring 0.5 g of the perfectly filtered hydrogel of iron(III) hydroxide in 2 ml of an alkali metal or ammonium sulphide solution at 22 $\pm$ 1° for 24 h, which was found to

be satisfactory for attaining equilibrium. The loss of sulphide ions from the solution was determined by iodimetric titration.

The uptake of the radionuclides under static conditions was studied by stirring 0.1 g of dry iron(II) sulphide with 10 ml of solution with ionic strength 0.1; the acidity of the solution was adjusted with 0.1 M nitric acid or 0.1 M sodium hydroxide solution.

Under dynamic conditions, columns with an I.D. of 5 mm containing 0.5 g of the sorbent were used, with a flow-rate of 0.5–1.0 ml·cm^{-2}·min^{-1}. Breakthrough of the given ions was determined by common drop reactions. The sorption of metallic ions was mostly studied on the unsieved samples with particle size from 5 to about 50 μm.

Preparation of iron(III) hydroxide hydrogel

To 100 ml of 3.5 M iron(III) chloride solution, previously cooled to 10°, were added 67 ml of 8 M carbamide solution and 167 ml of 3.5 M hexamethylenetetramine. The precipitate formed was shaken, giving a transparent red-brown solution, which was dispersed in 1.5 l of kerosene that contained 200 ppm of SPAN-80. After attaining perfect dispersion, the temperature of the emulsified solution was gradually increased until gelatinization occurred, with the formation of transparent microbeads of iron(III) hydroxide gel. The gel particles were then separated from the organic phase and washed with trichloroethylene and the hydrolysis was completed by treating the gel with aqueous ammonia solution (1:10) for 3 h. After thorough washing with distilled water, the gel phase was separated by vacuum filtration. The iron content in the washed hydrogel was 207.7 mg of Fe_2O_3 per gram of hydrogel, corresponding to the composition $Fe(OH)_3 \cdot 32H_2O$.

Preparation of spherical iron(II) sulphide

FS-I. After washing, the iron(III) hydroxide gel was dispersed in three times its volume of distilled water and gaseous hydrogen sulphide was introduced into the suspension for 3 h with constant stirring. The solid phase was then filtered off and dried in the air at 22°.

FS-II. A glass column was freely packed with the hydrogel and the opening was closed with a stopper fitted with a capillary as a gas outlet. The column was fixed in a fume-hood and gaseous hydrogen sulphide was passed through the system. The conversion of hydroxide into sulphide was easily followed by monitoring the movement of a relatively sharp black zone. When the presence of hydrogen sulphide was detected at the capillary end, the supply of gas was stopped and the column hermetically sealed at both ends. After 12 h, saturation with gaseous hydrogen sulphide was completed by passing the gas for 15 min, the gel was washed from the column with acetone, filtered off, washed with diethyl ether and dried under vacuum at 40–50°.

FS-III. A 100-g amount of iron(III) hydroxide hydrogel was dispersed in 400 ml of 1 M sodium sulphide solution and the suspension was left in a closed vessel for 24 h, with occasional stirring. The gel phase was then separated by decantation and washed with a previously boiled 3 % solution of ammonium nitrate, distilled water and acetone. Drying in vacuum was carried out in the same manner as with sample FS-II.

FS-IV and FS-IVa. The preparation was analogous to that for sample FS-III,

except that 1 M sodium hydrogen sulphide was used for the conversion. Sample FS-IVa is the washed but undried gel of sulphide and was kept in a closed vessel under a layer of 3% ammonium nitrate solution.

FS-V. The sample was prepared in an analogous manner to FS-IV, except that the conversion took place in an open vessel with constant stirring for 12 h. The sodium hydrogen sulphide solution was then exchanged and the suspension heated to 80° and slowly cooled. After washing with 3% ammonium nitrate solution, acetone and diethyl ether, the iron(II) sulphide was dried under vacuum.

RESULTS

Conversion of iron(III) hydroxide into the sulphide

The iron(III) hydroxide gel can be converted into the sulphide by treatment with gaseous hydrogen sulphide or with an alkali metal or ammonium sulphide solution. The degree of uptake of sulphide ions from solution in the gel phase can be estimated from Fig. 1, where the sulphur:iron molar ratio, Q, is plotted against the equilibrium concentration of sulphide ions in solution. It follows from the results that Q increases sharply with increasing equilibrium concentration of sulphide ions in solution when a sodium hydrogen sulphide solution is used, up to $Q \approx 1.5$, which then remains virtually unchanged. Analogous results were obtained by using an ammonium sulphide solution. The uptake from a sodium sulphide solution is slower and saturation can be expected to occur at an equilibrium sodium sulphide concentration close to 1 M. However, the results in Fig. 1 cannot be interpreted only in terms
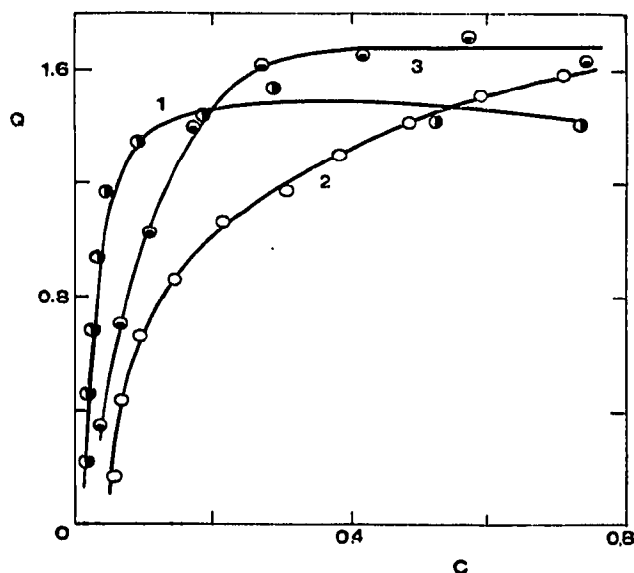

Fig. 1. Uptake of sulphide ions on iron(III) hydroxide hydrogel from solution. $Q =$ total $S:Fe$ molar ratio in gel phase; $C =$ equilibrium molar concentration of S^{2-} ions in solution. Curves: 1, NaHS; 2, Na$_2$S; 3, (NH$_4$)$_2$S. The ratio of aqueous to gel phase was 4 ml·g^{-1}.

of the exchange of hydroxyl groups for sulphide ions. The Q value also includes elemental sulphur, formed during the reduction of iron(III). Moreover, an increase in Q may occur if the gel phase contains a free solution of the sulphide. The results obtained, however, give the concentration of the particular sulphide ions at which the maximum conversion can be achieved. On the basis of these results, the conditions for the preparation of the individual samples of iron(II) sulphide, described under Experimental, were selected. The compositions of the individual samples are given in Table I.

TABLE I

COMPOSITION OF THE IRON(II) SULPHIDE SAMPLES

Fe_{tot} and S_{tot} denote total iron and sulphur content (mmole·g^{-1}): $Q = S_{tot}/Fe_{tot}$: A is sulphidic sulphur content determined analytically; B is the same, calculated from deposition of Ag^+ ions (see Table II); C is calculated from the relationship $S_{tot}/1.5$ (for samples with $Q \leqslant 1.5$) or $S_{tot} - 0.5$ Fe_{tot} (for samples with $Q > 1.5$).

Sample	Fe_{tot}	S_{tot}	Q	S^{2-} Content (mmole·g^{-1})		
				A	B	C
FS-I	5.05	1.57	0.31	—	0.35	1.05
FS-II	8.80	12.65	1.44	8.3	8.45	8.45
FS-III	5.79	5.09	0.89	—	2.57	3.40
FS-IV	6.47	11.51	1.78	8.1	8.20	8.27
FS-IVa	2.21	4.05	1.82	—	1.65	2.94
FS-V	6.61	10.78	1.63	7.1	8.20	7.48
2 FeS + S	9.62	14.43	1.50	—	—	9.62

When the iron(III) hydroxide gel is in contact with a sulphide solution, it turns black immediately. In thin layers, the particles have a greenish colour, especially in the first stage of the process. The mother liquor is black-green in colour. Only with sample FS-V was the mother liquor brown-red after heating, due to the presence of fine gel particles.

The converted gel is unstable towards atmospheric oxygen while wet. If the filtered-off gel is exposed to air, its exothermic oxidation to iron(III) hydroxide and elemental sulphur occurs. However, the hydrogel is relatively stable when covered with a layer of acetone or alcohol; the oxidation processes are also slow under water. Therefore, drying in vacuum was employed. Only sample FS-I, the yield of which was low (see Table I), could be dried in air.

Samples prepared by the action of gaseous hydrogen sulphide are relatively stable when dry and can be stored without difficulty in a well sealed vessel. On the other hand, samples prepared by treatment with alkali metal or ammonium sulphide solutions undergo oxidation quickly, even after drying. When they are exposed to air, oxidation begins within 1–2 min, accompanied by the release of heat. An argon atmosphere was therefore employed for manipulations with samples FS-III to FS-V. The weighed amounts were placed in a small volume of boiled distilled water, where no perceptible changes take place within several hours.

The dried samples are compact microbeads with a particle size of 5 to about 50 μm (see Fig. 2); bigger particles (about 2 mm in diameter) (see Fig. 3) can be pre-
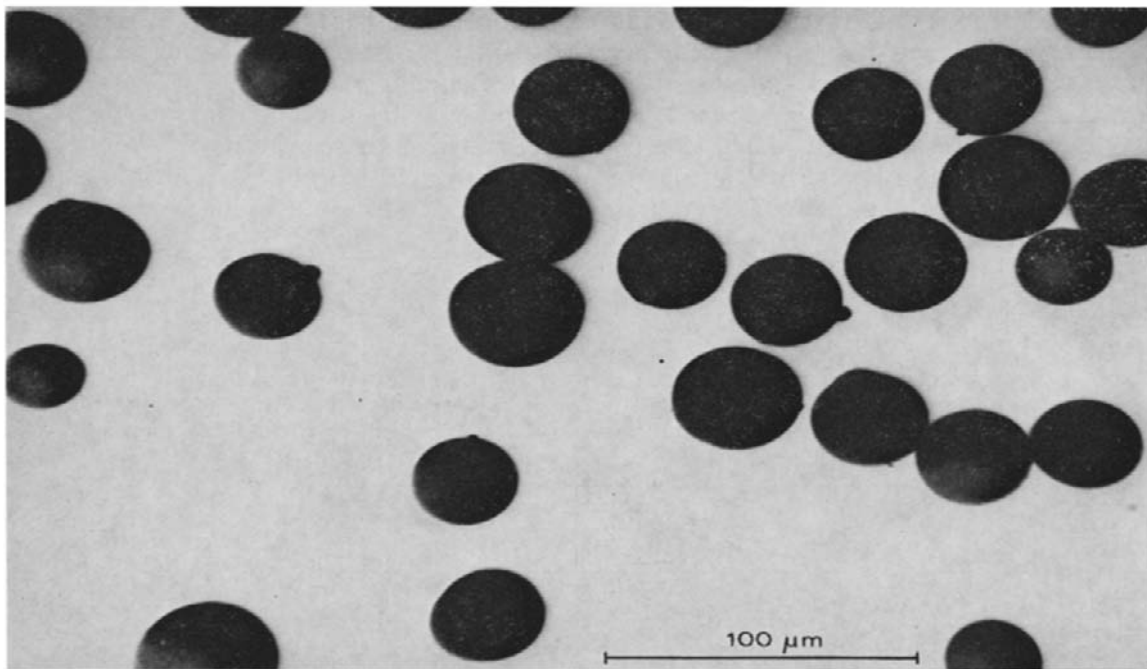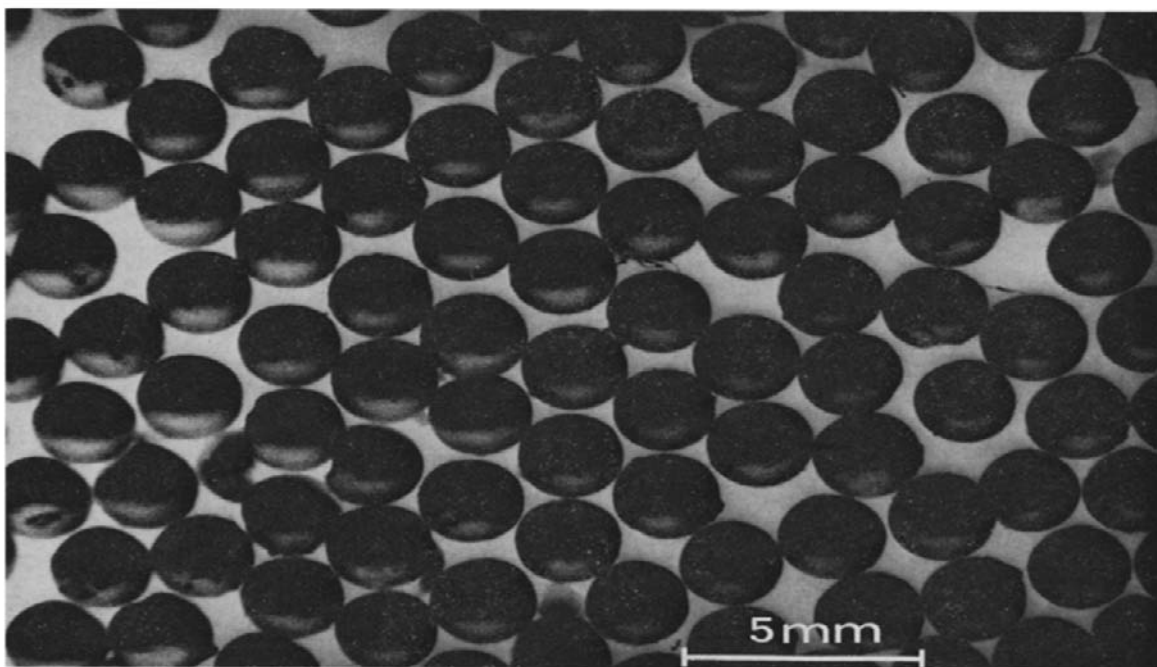
Fig. 2. Microphotograph of the sample FS-II.

Fig. 3. Macrophotograph of the sample FS-II obtained by conversion of hydrogel particles prepared in gelatinization column.
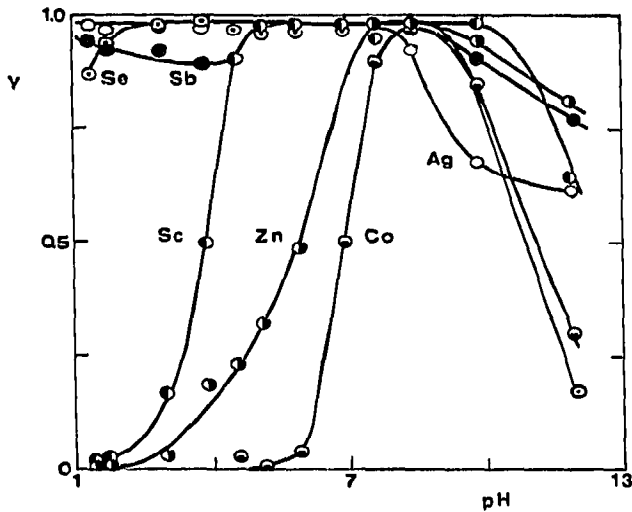
Fig. 4. Sorption of trace amounts of some elements on FS-I under static conditions. $Y =$ yield of radionuclide sorbed on sulphide. Sorption time, 3 h; phase ratio, 100 ml·g^{-1}.

pared in a continuously operating gelatinization column[13]. Samples obtained by using gaseous hydrogen sulphide are greyish black while the remainder, prepared by using solutions of sulphides, have an intense black colour.

Sorption of trace elements under batch conditions

The sorption of trace amounts of some elements on samples FS-I and FS-III is depicted in Figs. 4 and 5 as a function of the pH of the solution. Sample FS-I is stable over the whole hydrogen ion concentration range studied. Sample FS-III
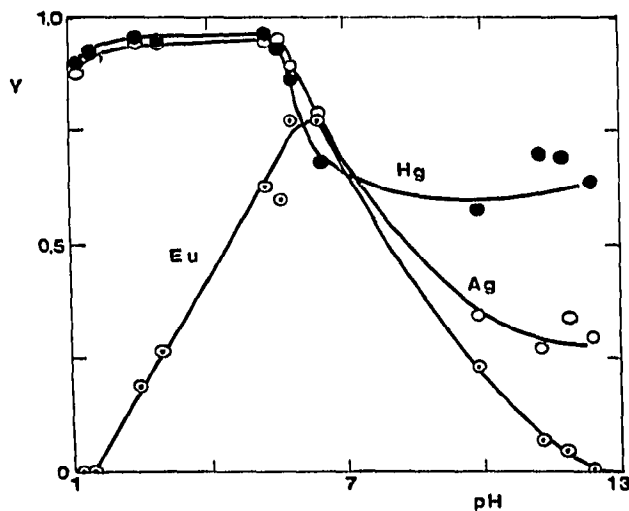

Fig. 5. Sorption of trace amounts of some elements on FS-III under static conditions as a function of pH. For conditions, see Fig. 4.

partially decomposes at pH < 3 and the solid phase then consists of a variable amount of dark precipitate, which is apparently a mixture of undecomposed sulphide, elemental sulphur and adsorbed silver and mercury sulphides.

It follows from the figures that an almost quantitative uptake of mercury, silver, antimony and selenium takes place in the acidic and neutral region. The other elements studied are sorbed predominantly in the neutral and weakly alkaline regions. On further increase in the pH, the sorption always decreases.

Sorption of trace elements under dynamic conditions

The behaviour of some metal ions, which form insoluble sulphides, on passage through a column of the samples studied can be seen from Table II, in which the uptake values up to breakthrough are shown. Except for ammoniacal solutions of copper, sorption is accompanied by displacement of Fe^{3+} ions, which, however, appear in the eluate only after passage of a certain portion of the sample. This value, expressed in milliequivalents of the adsorbed ion, is also given in Table II. Samples FS-I and FS-II are exceptions: Fe^{2+} ions appear immediately after passage of the column dead volume. Experiments with sample FS-III show that the solution volume that must pass through the column before Fe^{2+} ions break through is, to a certain extent, independent of the type of ion adsorbed (in the given case this volume is equivalent to the sorption of 1.8–2.0 mequiv.·g^{-1}).

The Fe^{2+} concentration in the eluate was not systematically determined. By

TABLE II

UPTAKE OF SOME IONS ON SPHERICAL IRON(II) SULPHIDE UNDER DYNAMIC CONDITIONS

Sample	Ion sorbed Me^{n+}	Me^{n+} concentration (mequiv.·ml^{-1})	Breakthrough uptake (mequiv.·g^{-1})	
			Fe^{2+}	Me^{n+}
FS-I	Ag^+	0.20	~0.17	0.70
FS-II	Ag^+	0.20	≤0.1	16.9
FS-III	Ag^+	0.20	1.96	5.14
FS-IV	Ag^+	0.20	1.56	16.4
FS-IVa	Ag^+	0.20	1.25	3.30
FS-V	Ag^+	0.20	1.65	16.4
FS-I	Hg^{2+}	0.20	~0.15	0.71
FS-II	Hg^{2+}	0.20	≤0.1	17.2
FS-II	Cu^{2+}	0.20	≤0.1	16.7
FS-II	Cd^+	0.216	≤0.1	16.1
FS-II	Pb^{2+}	0.196	≤0.1	15.0
FS-III	Hg^{2+}	0.20	1.89	5.98
FS-III	Cu^{2+}	0.20	2.18	4.94
FS-III	$Cu(NH_3)_4^{2+}$	0.20*	—	6.84
FS-III	Cd^{2+}	0.216	2.00	5.01
FS-III	Pb^{2+}	0.195	1.91	4.09
FS-III	Co^{2+}	0.251	1.55	1.66
FS-III	Ni^{2+}	0.196	1.76	2.26

* Concentration of ammonia in $Cu(NH_3)_4^{2+}$ solution is 1 mole·l^{-1}.

microtitrations of two or three fractions of the eluate, it was found that the exchange of ions is approximately equivalent when dry materials are used; only with undried hydrogel (sample FS-IVa) was an Fe^{2+} concentration equal to about half of the silver concentration injected, expressed in milliequivalents per millilitre, found.

The process of column saturation with ions of the elements studied can be easily observed visually by monitoring colour changes in the column, which gradually turns grey or, with cadmium, yellow. The boundary zone is very sharp, indicating sufficiently rapid reaction. From Table II, it also follows that the values of the breakthrough capacity for mercury, silver, copper and cadmium differ only slightly. With elements that form more soluble sulphides, the uptake gradually decreases. Because of the high self-diffusion coefficient of silver, it can be assumed that the breakthrough capacity values differ only little from the overall dynamic capacity. Therefore, the effective content of sulphide-sulphur in the individual samples was calculated from this value (see Table I, column B). The formation of binary salts[2] cannot be excluded during the uptake of mercury.

The FS-II sample was also used for the uptake of some heavy elements from aqueous solutions. One litre of industrial water containing 3 mg of mercury labelled with ^{203}Hg, 10 g of sodium nitrate and 1 ml of concentrated nitric acid was passed through a column of 1 g of iron(II) sulphide at a flow-rate of 10 ml·cm^{-2}·min^{-1}. The decontamination factor was determined to be $\geqslant 10^3$. The quantitative sorption of copper and cadmium was carried out in the same way.

In a similar manner to cadmium sulphide[14], the deposition of silver is not affected by the presence of sodium thiosulphate; a virtually identical capacity was found when a solution in 0.1 M silver nitrate and 0.2 M sodium thiosulphate was introduced into the column. This fact was utilized for the removal of silver from depleted photographic fixers: 25 l of used fixer were passed through the FS-IVa ion-exchange column with dimensions of 10 × 5 cm. No silver was detected in the eluate and from the height of the grey-black zone it was estimated that only 10–15% of the sorption bed was saturated.

DISCUSSION

The conversion of iron(III) hydroxide into the sulphide by treatment with gaseous hydrogen sulphide is analogous to the well known procedure for purification of coal gas[15]. Reduction of iron(III) takes place simultaneously with the substitution of hydroxyl groups, so that the resultant reaction is described by the equation

$$2\ Fe(OH)_3 + 3\ H_2S \rightarrow 2\ FeS + S + 3\ H_2O \qquad\qquad (1)$$
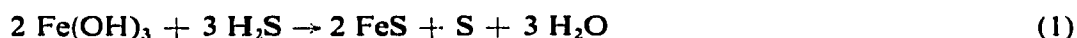
Hence it follows that ideally the final product consists of a mixture of the iron(II) sulphide gel and sulphur, with an S:Fe ratio of 1.5; the ratio of sulphide-sulphur to iron in the solid phase is unity. From Table I, it follows that sample FS-II most closely approaches this composition.

Conversion by means of alkali metal or ammonium sulphides in an alkaline medium probably follows another mechanism. Scholder (according to Remy[16]) assumes that thiohydroxy salts are formed by the action of alkali metal sulphides on solutions of salts of di- and trivalent iron; here sulphur can function as a partial sub-

stituent of hydroxyl groups in hydroxoferrites and hydroxoferrates, the compositions of which are expressed by formulae $Na_3SFe^{II}(OH)_3 \cdot 2H_2O$ (black-green) and $Na_8H_2O(OH)_6Fe^{III}SFe^{III}(OH)_6 \cdot H_2O$ (dark brown). Unanimous agreement about the existence of iron(III) sulphide has so far not been reached. Some workers consider that even in alkaline medium the trivalent iron is reduced[10].

It can be assumed that, disregarding probable differences in the structures of the individual samples, the conversion of the hydroxide form of a gel into the sulphide form is always accompanied by the reduction of trivalent iron, with simultaneous formation of elemental sulphur. Therefore, the samples obtained both by the conversion with gaseous hydrogen sulphide and by aqueous solutions of sulphides consist of iron(II) sulphide. This assumption is supported by the fact that the uptake of the ions studied is always accompanied by the elution of divalent iron. It is noteworthy that we always observed the black-green colour of the gel immediately after the addition of the alkali metal sulphide solution to the iron(III) hydroxide gel.

The chemical and physico-chemical properties of the sulphides prepared by precipitation indicate that they are not simple compounds of the MeS type but are more complex polymer systems[17]. During precipitation by the alkali metal sulphides, heteropolysulphides of the type $(MeS)_x(Me'S)_y$ may be formed. Under certain circumstances, $e.g.$ at a higher sulphur content in samples FS-III, -IV and -V than that which corresponds to the stoichiometry, it is indicated that these materials contain an alkali metal sulphide in spite of thorough washing, the sulphide being either adsorbed or chemically bound. It cannot be excluded that this fact accounts for their ready oxidation.

The properties of heteropolysulphides are best represented by a chain polymer structure, which can be expressed by the simplified formula
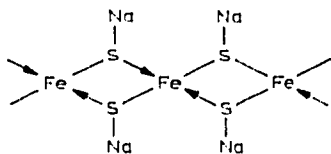
Then the sorption of chalcogenic ions (Me^{n+}) can be explained by the following mechanism. First, $Na-Me^{n+}$ exchange takes place according to the equation

$$G-SNa + 1/n \ Me^{n+} \rightarrow G-S(Me)_{1/n} + Na^+ \tag{2}$$
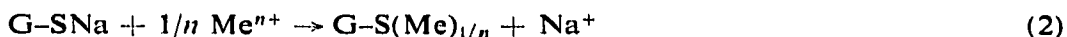
where G denotes the gel matrix, Me^{n+} the ion being sorbed and n its valency. In the second stage, ion exchange takes place, leading to the iron(II) ions being reduced to the solution according to the equation

$$FeS + 2/n \ Me^{n+} \rightarrow Me_{2/n}S + Fe^{2+} \tag{3}$$
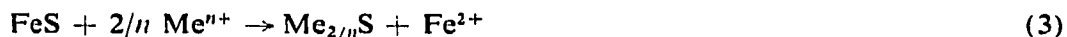
Only this type of exchange occurs with material prepared by the action of hydrogen sulphide, as is indicated by the appearance of Fe^{2+} ions in the eluate immediately after passage of the column dead volume when sample FS-II is employed.

With imperfectly converted gels, the existence of hydroxyl groups, which may also participate in the sorption process, must be taken into consideration. However, exchange reactions are only one of the ways in which heavy metals can be deposited. When iron(II) sulphide is in contact with solutions of salts of metals that are readily reduced, uptake by redox reactions may occur. For example, reduction to the elemental form apparently plays a role in the sorption of selenium and reduction to lower valency states in the uptake of antimony, arsenic, molybdenum, ruthenium and technetium. It has been found that these elements are also sorbed on the materials studied; however, no detailed results will be given here.

For the sorption of chalcogenic elements, the over-all sulphur content is unimportant, only the content of sulphide-sulphur being significant. However, it should be borne in mind that the reduction of iron(III) ions and the formation of iron(II) sulphide could be independent reactions. Thus the content of elemental sulphur in individual samples need not correspond to the iron(II) sulphide content. The S^{2-} content in the individual samples, calculated from the overall content of sulphur and iron, and given in Table I, is therefore only approximate.

The conversion with gaseous hydrogen sulphide appears to be the most suitable procedure for the preparation of spherical iron(II) sulphide. This reaction is very rapid, leads to quantitative conversion and the converted material need not be washed. The dry samples prepared in this way exhibited the highest stability towards oxidation by atmospheric oxygen. If necessary, the elemental sulphur present can be removed by extraction with dichloroethane or another suitable solvent. A disadvantage of this procedure may be the necessity for manipulation with gaseous hydrogen sulphide.

CONCLUSION

The results indicate that iron(II) sulphide, prepared by the conversion of iron(III) hydroxide hydrogel in the form of regular beads, can be used advantageously for the uptake of some chalcogenic elements. During the conversion and the subsequent treatment, the original spherical partical shape of the hydroxide hydrogel is not damaged; the partical size may vary in a wide range from about 10^{-3} to 1 mm.

The disadvantage of the easy oxidizability of the final product is compensated by the fact that iron ions are biologically harmless and the initial reactants are cheap. The most suitable preparation procedure seems to be conversion with gaseous hydrogen sulphide. The samples prepared are spherical solid particles, permitting the preparation of columns with a low hydro-dynamic resistance. The converted gel can also be used, without drying, as a hydrogel.

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