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THE NATURE OF SULPHUR COMPOUNDS IN WELL-ENCRUSTING SEDIMENTS

Abstract. The nature of sulphur compounds in well-encrusting sediments was determined using chemical and thermal analyses, X-ray diffractometry, IR spectroscopy, microscopic examinations in reflected light and electron microprobe analysis. The sediments in question have been found to contain iron sulphides, elementary sulphur and presumably also hydrated iron sulphates besides iron oxides, hydroxides and carbonates. The chemical composition of sulphides is similar to that of pyrite, $Fe_{0.84}S_{1.00} \cdot 1.12H_2O$, or troilite, $Fe_{0.85}S_{1.00} \cdot 0.18H_2O$. The sulphides generally have a collomorphous structure. Sulphate ions are largely adsorbed by iron oxides.

INTRODUCTION

Earlier studies of the chemical and mineralogical composition of sediments encrusting some wells in the area of Cracow (Ratajczak *et al.* 1977) have demonstrated their ferruginous nature. The total content of FeO and Fe_2O_3 has been found to be frequently higher than 80 wt. %. Iron minerals, specifically hydrated iron oxides, hydroxides and siderite, dominate in the composition of the sediments, giving them a bright rusty colour (Adamczyk *et al.* 1974; Ratajczak, Witczak 1974; Ratajczak *et al.* 1977). The analyses carried out so far have failed to show any significant amounts of sulphur compounds.

The observations made by the present authors during the disassembly

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of one of the well screens in the low terrace of the Vistula in Cracow have revealed that dark, frequently black, sediments and rusty-yellow ones occur side by side over a relatively short distance of 2—4 m. Black concentrations have been noted in the lower part of the screen. Their smell is characteristic of H_2S, and preliminary investigations have shown that they contain sulphur compounds. Rusty-coloured sediments precipitate in the upper part of the aquifer, and there is a transition zone between those two varieties.

The purpose of this paper was to define the nature of sulphur compounds in well-encrusting sediments. Investigations were carried out on a sample of black sediment derived from the lower part of the disassembled well screen from the area of Cracow.

RESULTS

Chemical analysis

The sediments studied were subjected to chemical analysis with special emphasis on the determination of the content of sulphur compounds. When SiO_2 was removed from the sample, the remainder was melted with Na_2CO_3 and Na_2O_2. The melt was dissolved in water with an addition of HCl, and total sulphur was determined as $BaSO_4$ using gravimetric method. The amount of sulphate sulphur was determined by decomposing the sample with a mixture of HCl and HF (1 : 1) which causes sulphide sulphur to volatilize as H_2S. The remaining part is suphate sulphur. Its content was estimated using gravimetric method with $BaSO_4$. The amount of sulphide sulphur was calculated as the difference between the contents of total and sulphate sulphur.

Table 1

Chemical analysis of the sample

Component	Weight %
SiO_2	1.52
Al_2O_3	1.46
Fe_2O_3	28.23
FeO	17.14
CaO	8.78
MgO	2.57
MnO	0.35
K_2O	0.08
Na_2O	0.39
SO_3	12.13
S^{-2}	3.95
loss on ignition	23.94
Total	100.54

Table 2

Content of sulphur compounds in well-encrusting sediments (weight per cent)

Author	Content	
	SO_3	S^{-2}
Gavrilko (1968)	1.35	7.55
Kommunar (1974)	0.3—0.6	
Marton, Sellyey (1971)	3.7—4.5	
Milihikier (1971)	0.4—0.8	
Ratajczak, Witczak (1974)	0.76—7.25	

The chemical composition of the sample is given in Table 1. It is evident from the results that the total content of FeO and Fe_2O_3 is lower than indicated by the earlier studies of well-encrusting sediments. It also appears that the FeO/Fe_2O_3 ratio is higher than observed so far. In the sediments studied earlier by the present authors this ratio varied from 0.01 to 0.22 (Adamczyk et al. 1974; Ratajczak, Witczak 1974; Ratajczak et al. 1977). Gavrilko (1968) and Milichikier (1971) gave a value of 0.40 and 0.03, respectively, whereas in the sample studied it was estimated at 0.61.

As appears from chemical analysis, iron oxides are the dominant constituent of the sediments studied. Worth noting, however, is a high content of sulphur compounds. The amount of sulphate and sulphide sulphur totals 16.08 wt. %. This fact seems to be significant because in the well-encrusting sediments studied by other authors (Table 2) sulphur was neglected altogether or its concentrations were much lower.

The analysed sample has been also found to contain elementary sulphur. Its presence was detected when determining the composition of an organic extract obtained in Soxhlet's apparatus. The X-ray diffraction pattern of this extract shows reflections typical of orthorhombic sulphur.

The results of chemical analysis of black well-encrusting sediments and the noted *anomalies* acquire significance when combined with observations made by Gavrilko (1968). This author noticed that in some wells the concentrations of SO_3 increased (up to 25 wt. %) towards the screen bottom at the expense of Fe_2O_3, whose content decreased in the same direction. This phenomenon was attended by a change in colour of the sediments from rusty to dark.

X-ray diffraction analysis

The investigations were carried out in a TUR M-61 diffractometer over the full angle range, using CoK_α radiation.

The X-ray diffraction pattern shows pronounced reflections of siderite (2.79, 2.34, 2.13 Å) and calcite (3.02 Å) (Fig. 2), whereas reflections of iron hydroxides, hydrated oxides, sulphides and sulphates do not allow an unequivocal identification of those compounds. This is due not only to partial coincidence of the reflections but also to the fine-dispersive form of the sediments (Ratajczak et al. 1977), which causes most reflections to be diffuse.

Nevertheless, the obtained d_{hkl} values yield some information regarding the mineralogical composition of the sediments studied. The presence of goethite and hydrated haematite can be inferred from the d_{hkl} values similar to those obtained for these minerals in earlier studies (Adamczyk et al. 1974; Ratajczak, Witczak 1974; Ratajczak et al. 1977). The reflection $d = 7.2$ Å evidences a high degree of hydration of goethite (Czuchrov et al. 1977). Weak and diffuse reflections 2.52, 2.25 and 1.97 Å suggest the presence of incompletely crystallized hydroxides of the $Fe(OH)_3$ type (Towe, Bradley 1967).

The presence of iron sulphides is indicated by the reflections $d_{hkl} = 5.05, 2.97, 2.64, 2.30, 2.08, 2.01$ Å; yet, because of the similarity of the d-spacings, it is difficult to define whether troilite, greigite or mackinawite is responsible for their appearance. It seems that the analysed
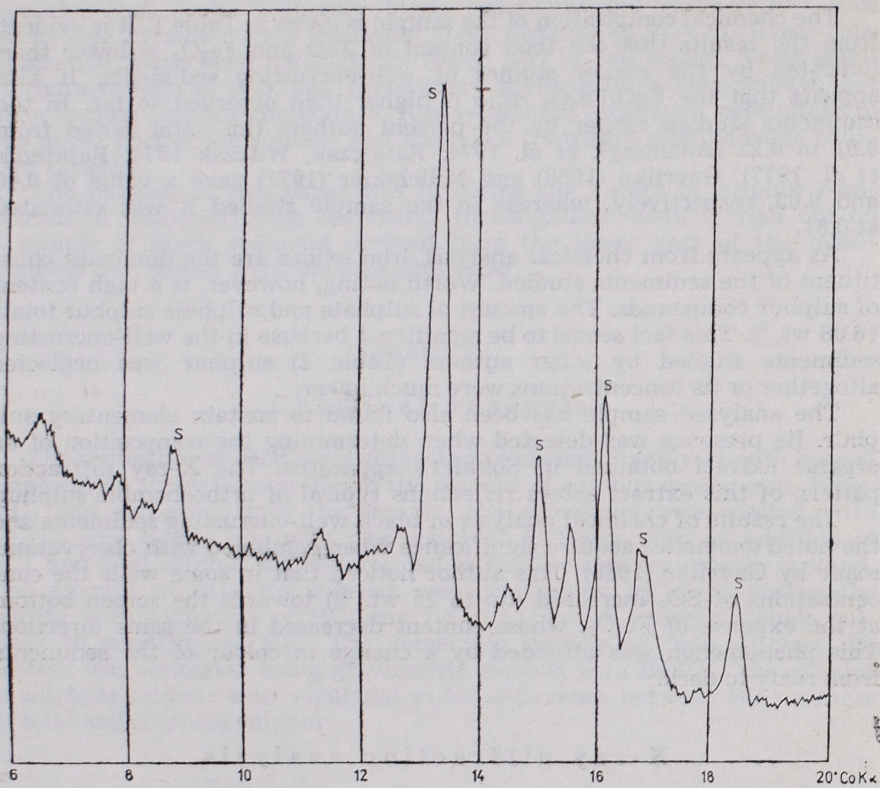
Fig. 1. X-ray diffractogram of extract obtainned in Soxhlet apparatus
S — sulphur

substance contains a mixture of iron sulphides. This observation would substantiate Ward's hypothesis (*fide* Joffe 1976) that iron sulphides are to be considered as one substance which assumes the form of various modifications, depending on the Fe : S ratio and the genetic conditions.

The reflections regarded by Kubisz (1964) as typical of hydrated iron sulphates coincide with reflections of other minerals present in the sediment. Hence their unmistakable identification is impossible. The reflection $d = 4.29$ Å is due to gypsum.

Thermal analysis

The sample was subjected to thermogravimetric analysis (Fig. 3). The interpretation of the TG curve presents some difficulties due to the coincidence of thermal peaks produced by the constituent compounds. Three ranges of weight loss are pronounced on the curve: *I* — 200—300°C, *II* — 400—700°C, *III* — 800—1000°C. The first and third range of weight loss have been already discussed by the authors in an earlier paper (Ratajczak
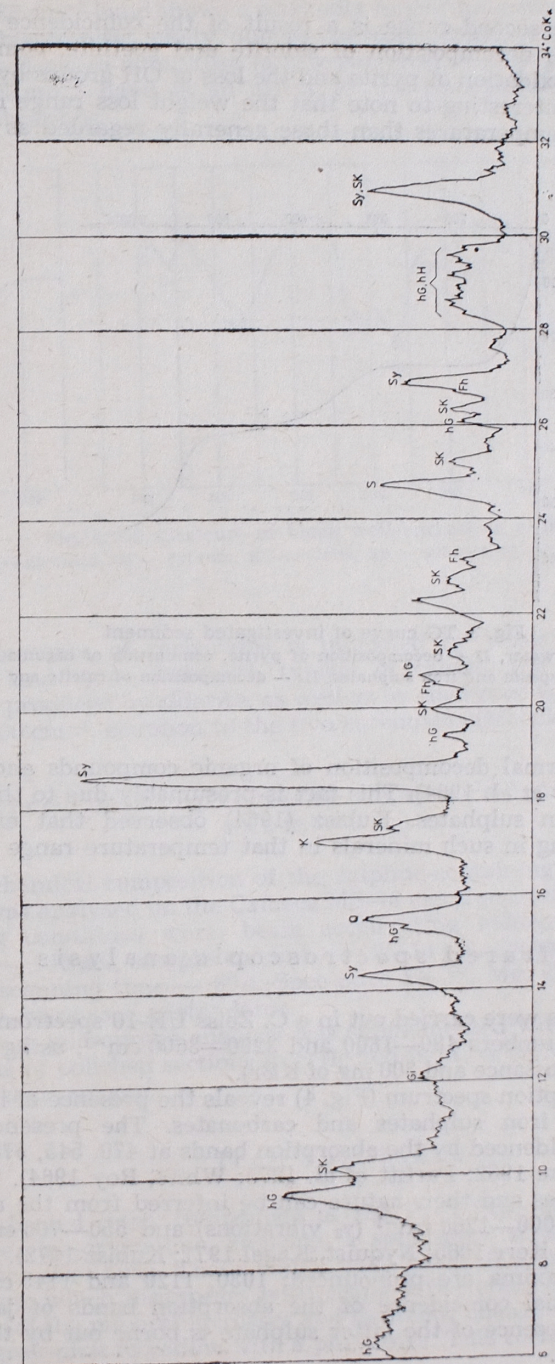
Fig. 2. X-ray diffractogram of black well-encrusting sediments

hG — hydrogoethite, hH — hydrohaematite, Fh — Fe(OH), Gi — gypsum, K — calcite, Sy — siderite, Sk — iron suphide, Q — quartz

et al. 1977). The second range is a result of the coincidence of several peaks due to the decomposition of siderite and goethite, combustion of organic matter, oxidation of pyrite and the loss of OH groups by basic iron sulphates. It is interesting to note that the weight loss range in question reaches higher temperatures than those generally regarded as limit tem-
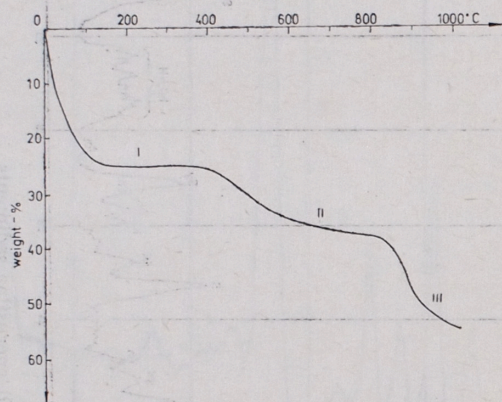

Fig. 3. TG curve of investigated sediment

I — loss of adsorbed water, *II* — decomposition of pyrite, combustion of organic matter, dehydration of goethite, gypsum and iron sulphates, *III* — decomposition of calcite and iron sulphates

perature for thermal decomposition of organic compounds and iron sulphates (Tsvetkov *et al.* 1964). This fact is presumably due to the presence of hydrated iron sulphates. Kubisz (1964) observed that endothermic reaction occurring in such minerals in that temperature range frequently exceeds 500°C.

Infrared spectroscopic analysis

Investigations were carried out in a C. Zeiss UR-10 spectrometer in the range of wave numbers 400—1800 and 3200—3600 cm^{-1}, using KBr disks (1.5 mg of the substance and 300 mg of KBr).

The IR absorption spectrum (Fig. 4) reveals the presence of iron hydroxides, gypsum, iron sulphates and carbonates. The presence of iron hydroxides is evidenced by the absorption bands at 470, 545, 578, 599, 803, 904 cm^{-1} (Moenke 1962; Parfitt *et al.* 1975; White, Roy 1964). The occurrence of sulphates and their nature can be inferred from the absorptions in the regions 1000—1200 cm^{-1} (v_3 vibrations) and 550—700 cm^{-1} (v_4 vibrations) (Adler, Kerr 1965; Nyquist, Kagel 1971; Kubisz 1972). In the first region, three maxima are pronounced: 1030, 1120 and 1145 cm^{-1}, being a result of partial coincidence of the absorption bands of jarosite and gypsum. The presence of the latter sulphate is borne out by the 670 and 1620 cm^{-1} bands.

The 1030 cm^{-1} band shows a markedly higher intensity than in standard spectra. This is most likely due to the coincidence with the absorption bands caused by an admixture (a few per cent) of amorphous silicates.

The 605 cm^{-1} band is an effect of the coincidence of gypsum and goethite vibrations.
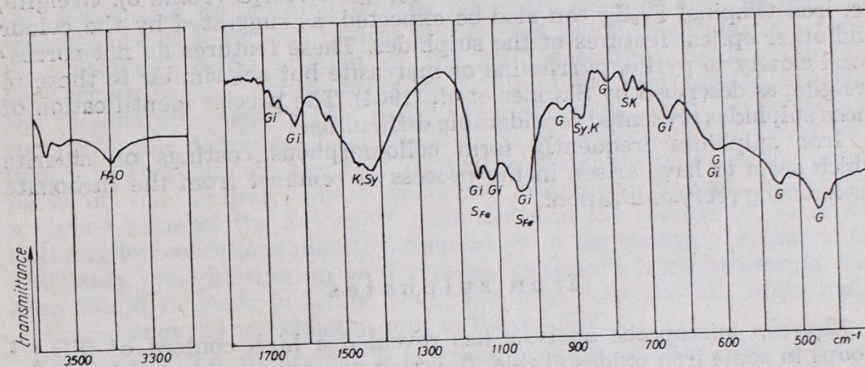

Fig. 4. IR spectrum of black well-encrusting sediments

G — goethite, Gi — gypsum, K — calcite, Sy — siderite, S$_{Fe}$ — iron sulphate

The presence of carbonates is indicated by weak absorptions v_4 — 712 cm^{-1} and v_2 — 880 cm^{-1}, typical of calcite, the maxima 740 and 868 cm^{-1} produced by siderite, as well as by the broad v_3 band in the range 1400—1500 cm^{-1}, common to the two carbonates (Moenke 1962).

Electron microprobe analysis and microscopic examinations

The chemical composition of the sulphur-containing compounds of the sample was analysed on the Cameca MS-46 electron microprobe. The probe operating conditions were: beam accelerating voltage — 20 kV; probe current — 140 μA; sample current — 10—14 μA, depending on the background; scanning time — 80 s. Spec-pure Fe, Si, Mg, Zn, as well as CaF$_2$ and Fe$_2$O$_3$ were used as standards.

Electron microprobe analysis was supplemented with microscopic examinations of polished sections in reflected light. A MIN-9 microscope was used for that purpose.

Iron sulphides

In reflected light, compounds of the Fe-S type have been detected. They are fine-crystalline, showing, a spherulitic structure and variable reflectance (20—40%). Those which have lower *R* values exhibit greater anisotropy, which disappears with rising reflectance. Simultaneously, the hardness of the mineral increases and its colour changes from grey through yellow-grey-pink to yellow with a pink tinge. This corresponds to a change

in the structure of sulphides from hydrotroilite ($FeS \cdot nH_2O$) to pyrite (FeS_2). The latter, however, failed to be detected by electron microprobe.

A typical, clearly collomorphous structure of iron sulphides is shown on Photographs 1, 2 and 3. Electron microprobe analyses (Phots. 4 *a*, *b*) indicate a chemical composition similar to that of pyrite — $Fe_{0.64}S_{1.00} \cdot 1.12 \cdot H_2O$ — or closer to troilite — $Fe_{0.85}S_{1.00} \cdot 0.18H_2O$ (Table 3). Greigite, i.e. iron tiospinel Fe_3S_4, can also be expected, as suggested by the colour and other optical features of the sulphides. These features do not correspond closely to pyrite, pyrrhotine or marcasite but are similar to those of greigite, as described by Skinner *et al.* (1964). The precise identification of those sulphides presented considerable difficulties.

Iron sulphides frequently form collomorphous coatings on siderite which seem to have arisen in the process of *removal* from the carbonate mass during recrystallization.

Iron sulphates

Electron microprobe analysis has revealed a high content of $[SO_4]^{-2}$ groups in some iron oxides (Table 3), which are presumably partly adsorbed and partly occur as an admixture of hydrated $FeSO_4$. This interpretation is suggested by the presence of elementary sulphur in iron oxides (Photographs 5 *a*, *b*), which fact was ascertained by microprobe investigations and borne out by X-ray diffraction analysis of the extract obtained in Soxhlet's apparatus.

The chemical composition of iron hydroxides (Table 3) differs from that of oxides in that the sulphur admixture is considerably smaller. This may be due to the loss of sulphur during recrystallization of the primary iron compounds precipitating in wells.

Both in iron oxides and hydroxides, sulphur admixtures induce changes in their reflectance and hardness, being also responsible for their anisotropy.

Table 3

Mineral components of investigated sediment resulting from electron-microprobe investigations

Sample No	Mineral component
	Hydrated oxides
4/1	$Fe_2O_{2.81}(SO_4)_{0.19} \cdot 1.61\ H_2O$
4/2	$Fe_2O_{2.96}(SO_4)_{0.04} \cdot 2.14\ H_2O$
4/3	$Fe_{1.99}Zn_{0.01}O_{2.63}(SO_4)_{0.37} \cdot 0.03\ H_2O$
	Hydroxides
4/A	$Fe_{1.00}O_{1.00}(OH)_{1.98}(SO_4)_{0.02}$
4/Al	$Fe_{0.99}Ca_{0.01}(OH)_{2.99} \cdot 0.49\ H_2O$
4/Cl	$Fe_{1.00}(OH)_{3.00} \cdot 0.95\ H_2O$
4/Dl	$Fe_{0.99}Ca_{0.01}(OH)_3 \cdot 1.38\ H_2O$
	Sulphides
94/B3	$Fe_{0.64}S_{1.00} \cdot 1.12\ H_2O$
94/B4	$Fe_{0.85}S_{1.00} \cdot 0.18\ H_2O$

DISCUSSION

Estimates of the redox potential at the definite pH and specified chemical composition of water solutions imbibing the well-encrusting sediments indicate that iron compounds showing varying degrees of oxidation can precipitate on working screens relatively close to one another. The co-existence of sediments typical of different redox conditions is a result of substantial differentiation of the hydrogeological field within the Quaternary rocks. This is particularly true of the first aquifer, in which the screens discussed in this paper were operating. Even in aquifers of inconsiderable thickness 5—10 m, the Eh of water usually drops with depth; in consequence, the Fe^{2+} content in water increases in the deeper parts of the aquifer, where reduction conditions prevail, and hence a higher value of the Fe^{2+}/Fe^{3+} ratio noted in the sediments. Variations in the redox conditions manifest themselves in the change of colour of the sediments precipitating on well screens. Dark and black sediments have been found in parts in which reduction conditions prevail, while rusty-coloured ones in the oxidation zone of the aquifer.

Studies of the mineralogical composition have revealed that black sediments contain iron sulphides, elementary sulphur and, most likely, hydrated iron sulphates (jarosites) alongside of iron oxides, hydroxides and carbonates. Iron sulphides are largely responsible for the colour of the sediments. From estimates of the average redox potential it appears that, in the case discussed, the conditions are not particularly favourable to the precipitation of iron sulphides. The latter compounds presumably owe their origin to organic matter present in the aquifer, which causes a local decrease in Eh, reducing the iron sulphates to sulphides. This process can be promoted by sulphur bacteria (Roshova *et al.* 1965, Bondarenko 1968, Płochniewski 1973). The bacterial activity gives rise to colloidal $FeS \cdot nH_2O$. Zyska (1977) noticed that bacteria reducing sulphates to sulphides cause corrosion of metals, and the black coatings which are formed have a strong smell characteristic of H_2S. He has found that iron sulphide accumulates not only in the corrosion products but also in the soil near the corroded pipes. Studies of Baas Becking, Kaplan and Moore (1960) have revealed that sulphur-reducing bacteria develop at pH 4.15—9.92 and Eh ranging from $+115$ to -450 mV. The above facts also account for the presence of elementary sulphur in the sediment. The process of formation of iron sulphides is in intimate association with a local increase in the con-centration of some other elements. In the case studied it has been found that, e.g., the contents of Cu, Co, as well as those of V and Mn in black sediments are, respectively, 5, 8 and 10 times higher than the concentration of those elements in rusty sediments. The experimental data of Roberts *et al.* (1969) support the possibility of occurrence of colloidal iron sulphides in well-encrusting sediments. It follows from those data that iron sulphides form at pH < 6, when the access of oxygen is cut off. Roberts has also noticed that such conditions promote the formation of elementary sulphur. It seems that diagenetic and aging processes, which give rise to pyrite-type sulphides from colloidal iron sulphides and whose role has been appreciated by Barner (1971), were not active in the case considered.

Sulphates, e.g. gypsum, have been detected in the sediments studied. Most of $[SO_4]^{-2}$ anions are free to migrate. Some of them are presumably

adsorbed by iron oxides. As shown by the studies of Rejman-Czajkowska (1972), the mobilization of sulphur compounds in Quaternary deposits follows the mobilization of iron compounds during the process of washing. Only a small part of sulphur compounds precipitates in the form of relatively sparingly soluble sulphates (gypsum). The remaining compounds keep the ability to migrate as long as the solution does not become oversaturated with sulphates due to the gradual loss of water. Investigations of Kroll and Swinarski (1964) have shown that iron compounds making up the aging series of hydroxides (i.e. the substances similar to those studied in this paper) are capable of combining with sulphur compounds. According to these authors, the binding activity of those compounds is significantly enhanced by the fine-grained texture of the sediments. This accounts for the presence of iron hydroxides with adsorbed $[SO_4]^{-2}$ anions (Table 3).

In his discussion of the genetic features of jarosites, Kubisz (1964) stated that these minerals form not only in rocks containing iron sulphides but also in those being within the range of activity of surface water. Their crystallization is also promoted by compounds of the $Fe(OH)_2$ type present in the solutions. It is evident, therefore, that these conditions are exactly the same as in the case of encrustation, accounting for the presence of iron sulphates in well-encrusting sediments.

REFERENCES

ADAMCZYK A., RATAJCZAK T., WITCZAK S., 1974: Hydrochemiczne warunki krążenia żelaza w utworach czwartorzędowych rejonu Włocławka. *Zesz. nauk. AGH Geologia* 22.

ADLER H. A., KERR P. F., 1965: Variations in infrared spectra, molecular symmetry and site symmetry of sulfate minerals. *Amer. Miner.* 50.

BAAS BECKING L. G. M., KAPLAN J. R., MOORE D., 1960: Limits of the natural environment in terms of pH and oxidation-reduction potentials. *Journ. of Geol.* 68.

BARNER R. A., 1971: Principles of chemical sedimentology. International Series in the Earth and Planetary Sciences.

[BONDARENKO T. P.] БОНДАРЕНКО Т. П., 1968: О растворении некоторых сульфидов в присутствии гуминовых и фульвокислот. Из-ство Наука, Москва.

[CHUKHROV F. V., GORSHKOV A. I., JERMILOVA L. P.] ЧУХРОВ Ф. В., ГОРШКОВ А. И., ЕРМИЛОВА Л. П., 1977: К минералогии железистых осадков депресии Бауэра (Тихий океан). Изд. АН СССР сер. геологическая I.

[GAVRILKO V. M.] ГАВРИЛКО В. М., 1968: Фильтры водозаборных, водопонизительных гидрологических скважин. Москва.

[JOFFE P. A.] ИОФФЕ П. А., 1976: О строении моносульфида железа $Fe_{1-x}S$ и химическом состоянии его компонентов. Геохимия I.

[KOMMUNAR G. M.] КОММУНАР Г. М., 1974: Исследование процессов химического кольматажа скважин и разработка методики прогноза снижения их производительности. ВНИН „Водгео". Москва.

KROLL Z., SWINARSKI A., 1964: Mechanizm wiązania siarkowodoru przez czyste tlenki i wodorotlenki żelaza. *Chemia Stos.* 8, 2.

KUBISZ J., 1964: Studium minerałów grupy ałunitu-jarosytu. *Pr. geol.* 22.

KUBISZ J., 1972: Studies on synthetic alkali-hydronium jarosites III. Infrared absorption study. *Miner. pol.* 3.

MARTON L., SELLYEY G., 1971: Elttömödött vizade kutek feltrarasanak tapasztaletei. Hidrol. *Közlöny* 3.

[MILIHIKIER A. T.] МИЛИХИКЕР А. Т., 1971: Осадкообразование в скважинах водопонижения. Москва.

MOENKE H., 1962: Mineralspektren. Berlin.

NYQUIST R. A., KAGEL R. O., 1971: Infrared spectra of inorganic compounds. New York and London.

PARFITT R. L., RUSSELL J. D., FARMER V. C., 1975: Confirmation of the surface structures of goethite (α-FeOOH) and phosphated goethite by infrared spectroscopy. *Jour. of the Chem. Soc.* 72.

PŁOCHNIEWSKI Z., 1973: Występowanie żelaza i manganu w wodach podziemnych utworów czwartorzędowych (na przykładzie wybranych obszarów północnej i centralnej Polski). *Biul. Inst. Geol.* 277.

RATAJCZAK T., WITCZAK S., 1974: Mineralogia i geochemia osadów żelazistych tworzących się w ujęciach podziemnych Włocławka. *Pr. miner.* 40.

RATAJCZAK T., WITCZAK S., KULGAWCZUK D. S., KRACZKA J., 1977: Badanie charakteru połączeń żelaza w osadach kolmatujących studnie. *Miner. pol.* 7, 2.

REJMAN-CZAJKOWSKA M., 1972: Wpływ oglejenia na migrację siarki. *Rocz-i glebozn.* 23, 1.

ROBERTS W. M. B., WALKER A. L., BUCHANAN A. S., 1969: The chemistry of pyrite formation in aqueous solution and its relation to the depositional environments. *Miner. Deposita* 4.

[ROSHKOVA E. V., KUZNIETSOVA E. T., VASILIEVA E. T.] РОЖКОВА Е. В., КУЗНЕЦОВА Е. Т., ВАСИЛЕВА Е. Т., 1965: Влияние бактеривильного процесса на образование эпигенетических сульфидных и других минералов в осадочных толщах. Литол. и пол. ископ. 4.

SKINNER B. J., ERD R. C., GRIMALDI F. S., 1964: Greigite, the thiospinel of iron; a new mineral. *Amer. Miner.* 49.

TOWE K. M., BRADLEY W. F., 1967: Mineralogical constitution of colloidal „hydrous ferric oxides". *Jour. Coll. and Interface Sci* 24, 3.

[TSVETKOV A. I., VALASHIHINA E. P., PILOJAN T. O.] ЦВЕТКОВ А. И., ВАЛЯШИХИНА Е. П., ПИЛОЯН Т. О., 1964: Дифференциальный анализ карбонатных минералов. Москва.

WHITE W. B., ROY R., 1964: Infra-red spectra—crystal structure correlations. II. Comparisson of simple polimorphic minerals. *Amer. Miner.* 49, 11—12.

ZYSKA B., 1977: Mikrobiologiczna ochrona metali. Wyd. Naukowo-Techniczne. Warszawa.

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CHARAKTER POŁĄCZEŃ SIARKI W OSADACH KOLMATUJĄCYCH UJĘCIA WODNE

Streszczenie

W niektórych ujęciach wodnych na terenie miasta Krakowa stwierdzono występowanie czarnych osadów kolmatujących te ujęcia. Osady wydzielały zapach typowy dla H_2S, co wskazywało na występowanie w nich połączeń siarki. Celem pracy było ustalenie charakteru tych połączeń. Dokonano tego przez zastosowanie badań chemicznych, termicznych, rentgenograficznych, spektroskopowych w podczerwieni a także obserwacji mikroskopowych i analizy w mikroobszarze.

Analiza chemiczna wykazała, że sumaryczna zawartość siarki siarczanowej i siarczkowej wynosi 16,08% wagowych próbki. Stosunek $FeO/Fe_2O_3 = 0,61$ jest dość wysoki jak na tego typu osady.

Na dyfraktogramie rentgenowskim próbki stwierdzono refleksy pochodzące od siarczków żelaza. Nie zdołano jednakże na ich podstawie sprecyzować, która z faz siarczkowych — troilit, greigit czy mackinawit jest za nie odpowiedzialna, gdyż podstawowe refleksy tych minerałów koincydują ze sobą. Wydaje się możliwe, że analizowana substancja zawiera różne siarczki żelaza. Nie stwierdzono refleksów pochodzących od uwodnionych siarczków żelaza. Badania rentgenograficzne ekstraktu organicznego osadów otrzymanego na aparacie Soxhleta wykazały obecność siarki rombowej. Potwierdziła to analiza rentgenospektralna w mikroobszarze. Wskazuje ona na występowanie wtrąceń siarki wśród tlenków żelaza.

Badania termograwimetryczne z racji nakładania się efektów termicznych pochodzących od różnych połączeń wchodzących w skład osadów nie wniosły wiele do znajomości ich składu fazowego.

W widmach absorpcyjnych w podczerwieni wyraźne są m.in. pasma pochodzące od grup $[SO_4]^{-2}$.

Przy pomocy badań mikroskopowych wykazano, że typową dla siarczków żelaza jest struktura kolomorficzna. Są one drobnokrystaliczne, cechują się zmiennym współczynnikiem odbicia światła. Ich analizy rentgenospektralne w mikroobszarze wskazują na skład chemiczny zbliżony do pirytu — $Fe_{0,85}S_{1,00} \cdot 1,12H_2O$ bądź też bardziej odpowiadający troilitowi — $Fe_{0,85}S_{1,00} \cdot 0,18H_2O$. W stadium pośrednim możliwe jest tworzenie się greigitu. Przemawia za tym stwierdzenie cech optycznych uważanych za charakterystyczne dla tego minerału. Wydaje się, że siarczki żelaza są głównym powodem ciemnego zabarwienia osadów kolmatacyjnych.

W badanych utworach wykazano także obecność siarczanów. Pewna ich część występuje w formie gipsu. Większość anionów SO_4^{-2} znajduje się w stanie wolnym i może migrować.

Z pomiaru wartości potencjału redox wynika, że w badanym przez nas przypadku nie ma specjalnych warunków do wytrącania się siarczków żelaza. Zapewne obecność ich jest efektem występowania w warstwie wodonośnej substancji organicznej. Wpływa ona na lokalne obniżenie wartości Eh, powodując redukcję siarczanów do siarczków żelaza. Proces ten może zachodzić pod wpływem bakterii siarkowych. Efektem tej działalności jest powstanie koloidalnego $FeS \cdot nH_2O$. Tą drogą powstaje także siarka elementarna rozpoznana w badanym materiale.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogram rentgenowski ekstraktu otrzymanego na aparacie Soxhleta
S — siarka

Fig. 2. Dyfraktogram rentgenowski czarnych osadów kolmatujących studnie
hG — hydrogetyt, hH — hydrohematyt, Fh — Fe(OH)₃, Gi — gips, K — kalcyt, Sy — syderyt, Sk — siarczek żelaza, Q — kwarc

Fig. 2. Krzywa termograwimetryczna badanego osadu
I — utrata wody zaadsorbowanej przez próbkę, II — rozkład pirytu, getytu, spalanie substancji organicznej, odwodnienie gipsu, utrata wody przez siarczany żelaza, III — rozkład kalcytu i siarczanów

Fig. 4. Spektrogram absorpcyjny w podczerwieni czarnych osadów wytrącających się w ujęciach wodnych
G — getyt, Gi — gips, K — kalcyt, Sy — syderyt, S_{Fe} — siarczan żelaza

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Przerosty kolomorficznych siarczków żelaza typu hydrotroilit — piryt (białe — Sk). Występują one w ziarnach syderytu (Sy) oraz rzadziej kalcytu (K). 1 nikol. Pow. × 240

Fot. 2. Drobnorozproszone nagromadzenia siarczków żelaza (Sk) w syderycie i w kalcycie. 1 nikol. Pow. × 240

Fot. 3. Skupienia siarczków (Sk) i uwodnionych tlenków żelaza (hO) oraz syderytu (Sy). 1 nikol. Pow. × 240

Fot. 4. a — Kolomorficzne siarczki żelaza (białe) w syderycie i w kalcycie (ciemnoszary). Pow. × 2000
b — Rozmieszczenie Fe, c — rozmieszczenie S

Fot. 5. a — Kolomorficzne skupienia uwodnionych tlenków żelaza zawierające inkluzje siarki. Pow. × 1000
b — Rozmieszczenie Fe, c — rozmieszczenie S

Хенрик КУХА, Тадеуш РАТАЙЧАК, Станислав ВИТЧАК

ХАРАКТЕР СОЕДИНЕНИЙ СЕРЫ В НАНОСАХ
КОЛЬМАТИРУЮЩИХ ВОДОЗАБОРЫ

Р е з ю м е

В некоторых водозаборах на территории г. Кракова были обнаружены чёрные наносы кольматирующие эти водозаборы. Из наносов неслась вонь характерная для H_2S, что дало основание предполагать присутствие в них соединений серы. Целью работы было установление характера этих соединений. Достигнуто этого путём использования химических, термических, рентгенографических, ИК-спектроскоповых исследований и микроскопических наблюдений с анализом в микрообъёме.

Химический анализ показал, что суммарное содержание серы в сульфатных и серных соединениях равно 16,08% по весу образца. Соотношение $FeO/Fe_2O_3 = 0,61$ относительно высокое для этого рода наносов.

На рентгеновской дифрактограмме образца обнаружено рефлексы вызванные сульфидными соединениями железа. Однако на их основании не удалось точно установить, которая из сульфидных фаз — троилит, грейгит или макинавит, их вызывает, так как основные рефлексы этих минералов совместно совпадают. Кажется возможным, что изучаемое вещество содержит разные сульфидные соединения железа. Не обнаружено рефлексов вызванных гидратированными сульфатами железа. Рентгенографические исследования органического экстракта наносов по

лученного в приборе Сокслета выявили присутствие ромбической серы. Подтвердил это рентгеноспектральный анализ в микрообъёме. Указывает он на присутствие включений серы среди окислов железа.

Термогравиметрические исследования ввиду наложения термических эффектов, вызванных разными соединениями входящими в состав наносов, не внесли почти ничего в дело познания их фазового состава.

В инфракрасных спектрах поглощения очень чётки, между прочим, полосы вызванные группами $[SO_4]^{-2}$.

При помощи микроскопических исследований было выявлено, что типической для сульфидных соединений железа является коломорфная структура. Эти соединения являются мелкокристаллическими, характеризуются непостоянным коэффициентом отражения света. Их рентгеноспектральные анализы в микрообъёме указывают на химический состав близкий к пириту — $Fe_{0,64}S_{1,00} \cdot 1,12H_2O$ или более близкий к троилиту — $Fe_{0,85}S_{1,00} \cdot 0,18H_2O$. В промежуточной стадии возможно образование грейгита. В пользу этого выступает установление оптических характеристик, которые считают свойственными для этого минерала. Кажется, что главным образом сульфидные соединения железа являются причиной тёмной окраски кольматирующих наносов.

В изучаемых веществах установлено тоже присутствие сульфатов. Какая-то их часть представлена гипсом. Большая часть анионов $[SO_4]^{-2}$ находится в свободном состоянии и имеет возможность миграции.

На основании измерений редокс-потенциала установлено, что в изучаемом нами случае, нет специальных условий для выпадания сульфидных соединений железа. Весьма возможно, что их присутствие является эффектом нахождения в водонасыщенном слое органических веществ. Эти вещества влияют на местное снижение значения Eh, что ведёт к редукции сульфатов до сульфидных соединений железа. Этот процесс может происходит из-за влияния серных минералов. Результатом этой деятельности является образование колоидного $FeS \cdot nH_2O$. Этим путём образуется тоже элементарная сера обнаруженная в изучаемом материале.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгеновская дифрактограмма экстракта полученного в приборе Сокслета:
S — сера

Фиг. 2. Рентгеновская дифрактограмма чёрных наносов кольматирующих колодцы:
hG — гидрогетит, h — гидрогематит, Fh — Fe(OH)₃, Gi — гипс, K — кальцит, Sy — сидерит, Sk — сульфидное железо, Q — кварц

Фиг. 3. Термогравиметрическая кривая изучаемого наноса:
I — потеря воды поглощённой образцом, II — распад пирита, гетита, сгорание органического вещества, дегитратация гипса, потеря воды сульфидными соединениями железа, III — распад кальцита и сульфатов железа

Фиг. 4. ИК-спектр поглощения чёрных наносов, которые выпадают в водозаборах:
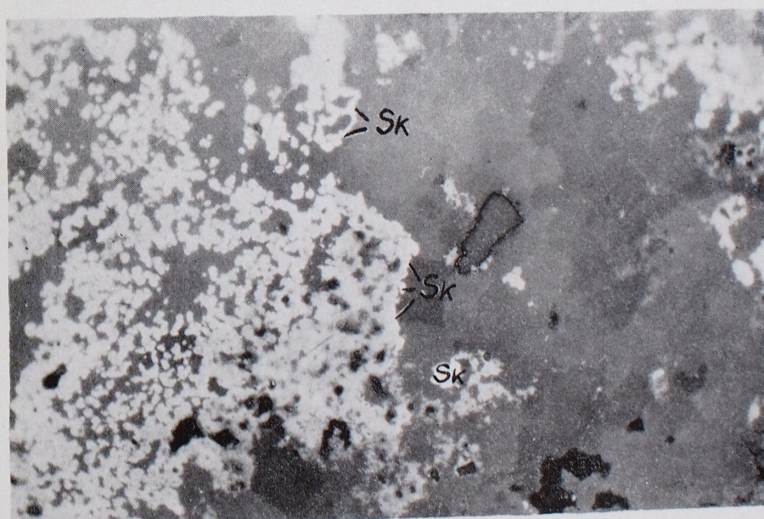G — гетит, Gi — гипс, K — кальцит, Sy — сидерит, S_Fe — сулифдное железо

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото.1. Прослойки коломорфных сульфидных соединений железа типа гидротроилита-пирита (белые — Sk). Присутствуют они в зернах сидерита (Sy) и реже кальцита (K). 1 николь. Увел. × 240

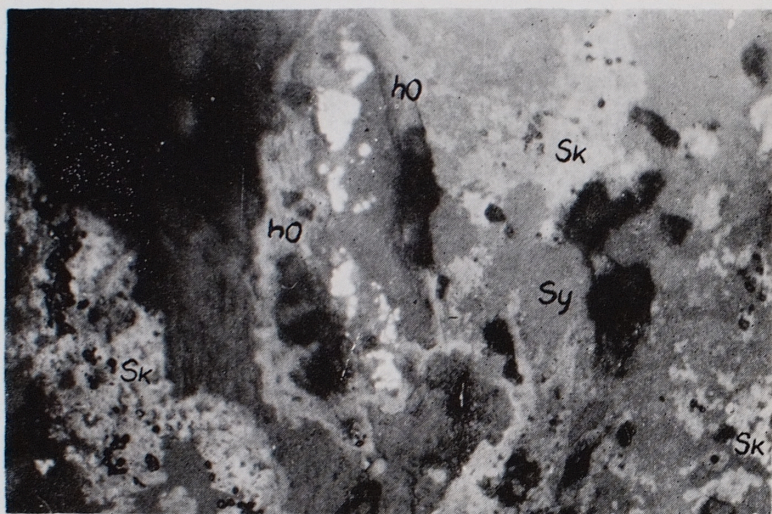Фото. 2. Мелкодиспергированные скопления сульфидных соединений железа (Sk) в сидерите и кальците. 1 николь. Увел. × 240

Фото. 3. Скопление сульфидных соединений (Sk), гидротированных окислов железа (hO) и сидерита (Sy). 1 николь. Увел. × 240

Фото. 4. a — Коломорфные сульфидное соединение железа (белые) в сидерите и кальците (тёмно-серый). Увел. × 2000
b — Расположение Fe, c — расположение S

Фото. 5. a — Коломорфные соединения гидратированных окислов железа, содержащие включения серы. Увел. × 1000
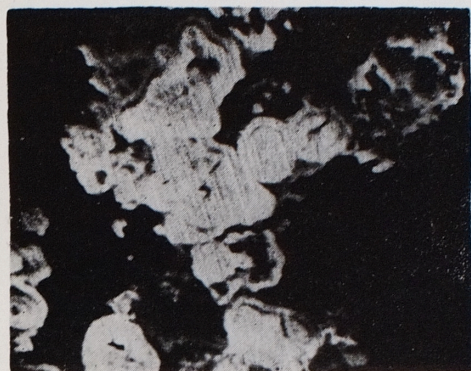b — Расположение Fe, c — расположение S
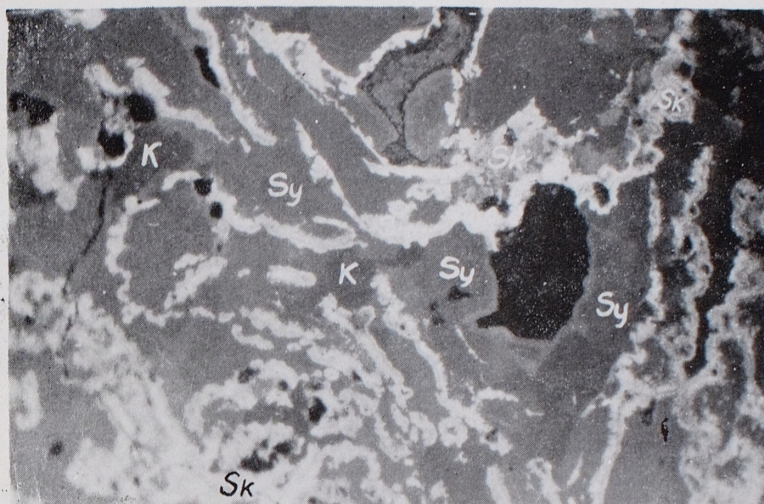
Phot. 1. Intergrowths of collomorphic iron sulphides of hydrotroilite — pyrite (white — Sk) type occurring on siderite (Sy) and calcite (K) grains, 1 nicol. Magn. × 240
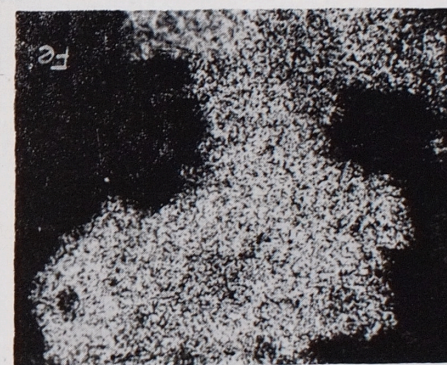

Phot. 2. Iron sulphides (Sk) disseminated in siderite and calcite grains. 1 nicol. Magn. × 240

Henryk KUCHA, Tadeusz RATAJCZAK, Stanisław WITCZAK — The nature of sulphur compounds in well-encrusting sediments

Phot. 3. Aggregates of iron sulphides (Sk) and hydrated oxides (hO) and of **siderite** (Sy). 1 nicol. Magn. × 240

Henryk KUCHA, Tadeusz RATAJCZAK, Stanisław WITCZAK — The nature of sulphur compounds in well-encrusting sediments
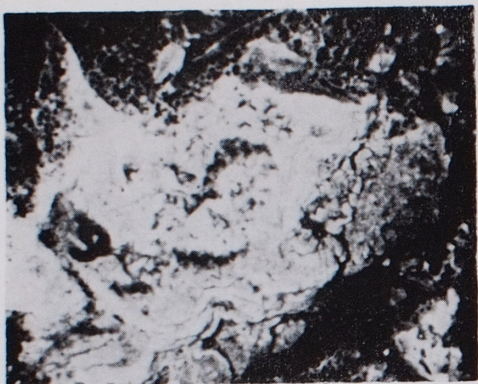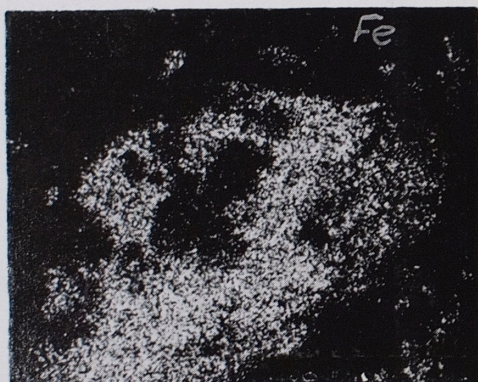
Phot. 4. a — collomorphic iron sulphides (white) in siderite and in caltice (dark grey). Electron absorption image. Magn. × 2000. b — distribution of Fe, c — distribution of S

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PLATE IV

Phot. 5. a — collomorphic aggregate of hydrated iron oxides containing an inclusion of elementary sulphur. Electron absorption image. Magn. ✕ 1000. b — distribution of Fe, c — distribution of S

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