

## Processes Occurring at the Decomposition of Sulphide Ores

First Communication

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Many authors have dealt with the processes occurring in the oxidating and cementating zone. *Schneiderhöhn* (1) was the first to report the results of these investigations in detail, whereas *Smirnov* (2) has recently summarized in his work published in 1951 the interpretations so far known in this field.

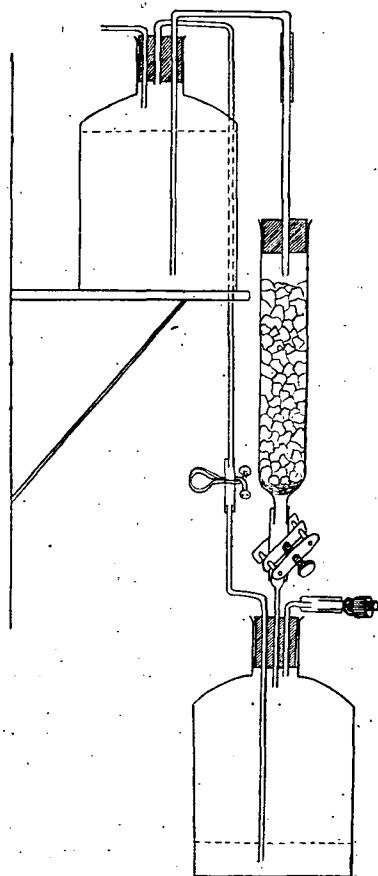
In the course of the investigations certain writers establishments were mostly of qualitative character concerning the oxidation and solubility of the different sulphide ores. In spite of the many experiments relatively few exact quantitative data are available. Especially investigations with pure substances, under well defined experimental conditions, systematically performed are lacking. In any case the latter condition — concerning the purity of the substance — is fairly difficult because in most cases a small amount of mechanical or isomorphic impurities must be taken into account. However, in spite of this we did not carry out our experiments with artificial pure sulphides because the size of the granules, as well as the other differences existing between the artificial and natural sulphides would lead to quite varying results with artificial sulphides than with the natural ones, apart from the fact of our aim being the examination of the behaviour of the natural sulphide ores. For example the solubility of artificial PbS in pure water at 18°C  $4 \cdot 10^{-6}$  mol/l, the solubility of artificial ZnS under similar conditions is  $70 \cdot 10^{-6}$  mol/l. Whereas that of natural galena and sphalerite is  $1 \cdot 10^{-6}$  and  $7 \cdot 10^{-6}$  mol/l, respectively (3). Thus it was found desirable to carry out our investigations with natural sulphides, to attempt also in this manner to reproduce as much as possible the actual changes taking place in nature. The more so since the composition of the naturally occurring sulphides usually does not correspond to the ideal formula.

In the summer 1942–44 on touring the mining district of Satu-Mare (Roumania) — Baia Mare, Baia Sprie, Herja etc. — the question was raised to investigate chemically and electro-chemically the mining-waters, examining their composition, conductivity and pH in each level to compare the experiences with the results of the examinations of the different ores contained in each level enabling conclusions to be drawn concerning the correlation between the mining-water and the changes occurring in the substance of the ore-lodes and reversely to establish, how the composition of the mining-water as well as its other properties change in relation to the composition of the ore-lodes.

Thus our initial examinations carried out in 1951 aimed at creating, artificially, conditions which can be found in nature in order to observe the processes occurring in the sulphide ore-deposits, for the elucidation of the kind and particularly the extent of changes which must be taken into account.

Our task was to accomplish the following investigations: as the fact of the ores occurring alone or associated with other ores influences their solubility, the pH, conductivity, change in free sulphuric acid and total sulphate content, as well as the ratio of the ferrous and ferric iron content of the solutions and finally at the end of the experiment the amount of Zn, Fe, Cu, Mn contained in the circulating solutions of the various ores was investigated, partly in homogeneous ore-debris and partly in ore-mixtures grouped as they can also be found in nature. Finally the changes which might be observed on the surface of the ore-debris were also examined.

For the sake of simplicity the pure ores and ore-mixtures investigated will be denoted with a number and in the following this number will be given.



Pure ores:

1. galena
2. sphalerite
3. pyrite
4. tetrahedrite
5. chalcopyrite

Ore-mixtures:

6. pyrite-chalcopyrite-sphalerite
7. galena- " "
8. " " pirrhotite
9. tetrahedrite " "
10. " pyrite "

Fig 1.

These are termed „pure“ because the used galena contains a small amount of mechanical impurities as sphalerite, pyrite and in turn sphalerite contains galena as mechanical impurity and pirrhotite as isomorphic impurities. Pyrite and tetrahedrite contain chalcopyrite, and with the exception of pyrite, each „pure“ ore contains manganese too. Only chalcopyrite showed ideal purity, containing a very slight amount of manganese.

In the course of the experiments the same amount of approximately 5 liters of the solution was constantly circulated through the ore-debris (300—350 g) in the tube. The solution steadily sickered through the debris and the sampling of the solutions could be carried out without taking the equipment into pieces. The examinations were made at room temperature. The circulating solution used was approximately 0.05 N sulphuric acid, the free sulphuric acid of which corresponds, according to Emmons and Farrington, (4) to the average free sulphuric acid content of the 42 mining-water analyses taken from sulphide ore-deposits. The circulation was started in June. The 5 l solution sickered through the debris in about 10 days, i. e. till the last sampling the solution sickered about twenty times through the debris, the latter was used for the determination of the Fe, Mn, Cu, Zn content of the solutions. The dates of the sampling:

Starting of the circulation:	June 25, 1951.
I. Sampling	July 28,
II.        „	August 4,
III.       „	August 13,
IV.        „	August 30,
V.         „	September 16,
VI.        „	October 23,
VII.       „	January 15, 1952.

The purpose of our investigations was the establishment of the behaviour of the examined ores and ore-mixtures from the point of view of their solubility and oxidation. In spite of it not being possible to attain granules of exactly the same size in the investigated sulphides — the differences influence the solubility to a great extent — as well as that the surfaces of the ores affected by the circulating solutions are not either quite identical, yet the measuring of the pH, conductivity, the examination of the changes of the free sulphuric acid and the whole sulphate content renders it after all possible to establish a sequence with respect to the oxidating and dissolving liability of the different ores and ore-mixtures. A further difficulty is that immediately after the oxidation and dissolving, respectively, further processes take place in the solution, which run down in different direction, their complexness rendering a clear impression and observation the details of the different processes, difficult and uncertain. The solubility is very much affected by the mechanical or isomorphic impurities of the examined substance which has been exhibited in many instances, particularly in the case of pyrite or sphalerite.

The following tables demonstrate the pH and conductivity values, as well as the results of the estimations of free sulphuric acid and the whole sulphate contents measured on the different samples:

Table 1.

*The change of the pH values.*

	I.	II.	IV.	V.	VI.	
	s a m p l i n g					change during the examination
1.	1.80	1.90	1.98	2.40	2.30	+ 0.50
2.	1.80	1.90	1.95	2.50	2.30	+ 0.50
3.	1.79	1.80	1.85	2.30	2.30	+ 0.51
4.	1.78	1.80	2.30	2.60	2.70	+ 0.92
5.	1.79	1.80	1.80	2.10	2.10	+ 0.31
6.	1.78	1.75	1.70	2.10	2.20	+ 0.42
7.	1.78	1.80	1.80	2.30	2.30	+ 0.52
8.	1.78	1.80	2.00	2.40	2.60	+ 0.82
9.	1.88	1.92	2.70	2.70	2.80	+ 0.92
10.	1.80	1.90	2.20	2.60	2.90	+ 1.10

Table 2.

*The change of the specific conductivity.*

	I.	II.	IV.	V.	VI.	
	s a m p l i n g					change during the examination
1.	0,0086	0,0083	0,0077	0,0071	0,0070	— 0.0016
2.	84	81	75	71	67	— 0.0017
3.	96	94	90	88	83	— 0.0013
4.	98	86	48	43	43	— 0.0055
5.	101	98	98	98	98	— 0.0003
6.	106	105	101	100	97	— 0.0009
7.	99	95	87	85	74	— 0.0025
8.	101	93	64	49	34	— 0.0067
9.	83	68	40	35	33	— 0.0050
10.	90	79	77	69	35	— 0.0055

Table 3.

*The change of the whole sulphate, free sulphuric acid, and bound sulphate content.*

$a$  = whole sulphate content  $SO_4$  g/l,  $b$  = free sulphuric acid content  $SO_4$  g/l,  $c$  = free sulphuric acid content  $H_2SO_4$  g/l,  $d$  = bound sulphuric acid content  $SO_4$  g/l.

	I.	II.	IV.	V.	VI.	change during the examination			
	s	a	m	p	l	i	n	g	
1.	<i>a</i> — 2.060	2.070	2.073	2.073	2.073				+0.013
	<i>b</i> — 1.844	1.767	1.612	1.624	1.481				—0.363
	<i>c</i> — 1.883	1.805	1.646	1.659	1.513				—0.370
	<i>d</i> — 0.216	0.303	0.461	0.449	0.592				+0.376
2.	2.087		2.185		2.289				+0.202
	1.776	1.759	1.620	1.669	1.526				—0.250
	1.814	1.796	1.655	1.705	1.559				—0.255
	0.311		0.565		0.763				+0.452
3.	2.591	2.653	2.787	2.872	2.989				+0.398
	2.116	2.090	1.955	1.915	1.856				—0.260
	2.161	2.134	1.997	1.956	1.896				—0.265
	0.475	0.563	0.832	0.957	1.133				+0.658
4.	2.381	2.404	2.418	2.429	2.437				+0.056
	2.170	1.866	0.771	0.616	0.464				—1.706
	2.216	1.906	0.788	0.629	0.474				—1.742
	0.211	0.538	1.647	1.813	1.973				+1.762
5.	2.241		2.255		2.255				+0.014
	2.071		2.053		2.048				—0.023
	2.115		2.097		2.092				—0.023
	0.170		0.202		0.207				+0.037
6.	2.521	2.546	2.569	2.591	2.611				+0.090
	2.240	2.233	2.214	2.196	2.179				—0.061
	2.288	2.280	2.261	2.243	2.224				—0.064
	0.281	0.313	0.355	0.395	0.432				+0.151
7.	2.283	2.283	2.283	2.283	2.283				0.000
	2.090	1.999	1.910	1.866	1.652				—0.438
	2.134	2.042	1.951	1.906	1.687				—0.447
	0.193	0.284	0.373	0.417	0.631				+0.438
8.	2.269	2.269	2.269	2.269	2.269				0.000
	2.210	2.058	1.723	1.375	1.035				—1.175
	2.257	2.102	1.760	1.404	1.057				—1.190
	0.059	0.211	0.546	0.894	1.234				+1.175
9.	1.974	1.974	1.974	1.974	1.974				0.000
	1.856	1.656	1.570	1.481	1.196				—0.660
	1.896	1.691	1.604	1.513	1.222				—0.674
	0.118	0.318	0.404	0.493	0.778				+0.660
10.	2.227		2.297	2.325	2.367				+0.140
	1.933	1.669	1.303	1.196	1.106				—0.827
	1.974	1.705	1.331	1.222	1.130				—0.844
	0.294		0.994	1.129	1.261				+0.967

Considering that the changes of the different ores due to oxidation and dissolving could only be investigated at the end of the experiment — on taking the equipment into pieces — in the course of the experiments the changes of the solutions visible by the naked eye where also observed in addition to the measurements.

The results of the measurement show that in sampling No. I. the pH also ranged between 1.78—1.80 in the case of ores and ore-mixtures but for mixture No. 9., which also exhibited in this case a relatively high — 1.88 — value. This mixture is mentioned because it was the solution in which the separation of iron hydroxide began for the first time to a great extent. This was followed by the solution circulating through mixture No. 10., the pH of which also showed a relatively quick shift and subsequently by the hydrolysis of No. 8., the change of the pH being less great than that of the aforementioned ones, however, relatively showing still a strong shift towards the weekly acidic character. Solution No. 7. merely exhibited a light yellowish colourization, whereas solution No. 6. remained quite clear. Hydrolysis could not either be detected in the solutions circulating through pure ores, at the most towards the end of the experiments a very slight yellowish colourization could be noticed in the solutions of tetrahedrite, sphalerite and galena. Among the pure ores the pH of the solution of tetrahedrite shows, as compared to the others a great change, the pH change of the sphalerite — and galena solutions is fairly similar, just as the change of the conductivity of their solutions also resembles to a great extent.

The change in conductivity is caused in the first place by the change of the free sulphuric acid content. The conductivity of the solutions diminish constantly to a smaller or greater extent. Of the pure ores the solution of chalcopyrite shows the smallest change, whilst the greatest decrease could be observed in the tetrahedrite solution, like in the case of the pH measurements the pH of this solution also rose to the greatest extent, at least is the case of pure ores. Among the mixtures at the first measurement the conductivity of No 9. was the lowest and at samplings I. and II. also this solution showed the greatest diminution, its pH being the highest. The subsequent decrease in order of magnitude could be observed in solution No. 10. the pH of which also remained lower than that of the previously mentioned ones, which was followed in sequel of order of magnitude by solution No. 8. The separation of the iron, occurring comparatively shortly after the starting of the circulation (it could already be observed at sampling III.) in solution No. 9., exhibited initially the greatest decrease in change of conductivity, and the greatest rise in change of pH, its free sulphuric acid content being also the lowest. The hydrolysis of the other solutions could be observed in the sequel mentioned above: solution No. 9. was followed by No. 10. and this by No. 8. in which solution, however, the extent of the separation of the iron soon exceeded that observed by the aforementioned two solutions. I. e. at the initial stage the sequel based on the conductivity measurements corresponds in these ore-mixtures with that based on the pH

measurements, which in turn is in complete agreement with the empirical fact, with the sequel in time of the hydrolysis of the solutions.

At the end of the experiment the iron content of the separated and sedimentated precipitate was: in solution No. 8. 4.317 g, in No. 9. 2.052 g, in No. 10. 0.4505 g Fe.

It can, however, not be stated that the hydrolysis of the solutions, the separation of the colloidal iron precipitate following the setting in of the hydrolytic equilibrium, the precipitation of the iron hydroxide as gel only depend upon the free sulphuric acid content, pH, conductivity of the solutions, i. e. that these only determine the processes running down in the solutions, as the solutions of tetrahydrate did not show any tendency to hydrolyse, although its conductivity already showed at the IV. sampling a greater decrease than solutions No. 8, 9., 10., its pH also being higher than that of No. 8. and 10. and its free sulphuric acid content remaining far lower than that of the aforementioned solutions. In this respect it should still be mentioned that the hydrolysis of the solutions and its great progress during our previous experiments could only be experienced in solutions circulating through ore-mixtures, whereas in pure ores, as in the mentioned tetrahydrate, if they also attained the different (pH, conductivity, sulphuric acid content) values, under which condition a strong iron separation could be observed in the solutions of the ore-mixtures, the hydrolysis did not set in, or only to a quite minimal extent colouring the solution very faintly, but did not precipitate an iron hydroxide gel. Thus the fact that an ore is alone or in contact with other ores does not only influence the solubility of the different ores — as will be still discussed later — but also plays a role in the processes running down in the solutions, as was seen in the case of the precipitation of gel iron hydroxide too. As, if only the pH, the conductivity, the amount of free sulphuric acid would determine the starting and extent of the hydrolysis of the solution a strong iron separation would have had in any case to be observed in the solution of tetrahydrate, owing to the reasons mentioned above. In the pyrite solution iron separation could not either be observed. At the same time the solution circulating through mixture No. 10. — consisting of tetrahydrate and pyrite — showed an intensive colourization directly after that of solution No. 9. and the separation of iron hydroxide started very soon. In the tetrahydrate solution ferrous iron dominated, whereas in solutions 8., 9., 10. ferric iron was predominant. The detailed examination of the conditions of the iron hydroxide separation are essential and will be dealt with in a later work, as the same separation of iron hydroxide gel can also be observed in nature leading to the formation of limonite deposits.

At the establishment of the dissolution of the ore, as well as at the setting up of the sequel the decrease of the free sulphuric acid content cannot only serve as a base, because at the simple dissolution of the ore the sulphuric acid diminishes and forms simultaneously owing to the oxidation, furthermore the ferric sulphate and copper sulphate also exert a dissolving action on the ores. The sequel can

rather be based on the comparison of the bound sulphate amounts of the solutions, although in this case it is also possible that one of the ores dissolves to a greater extent, than was observed by us on determining the bound sulphate quantities contained in the solutions, as the latter amount and its increase, respectively, can be diminished by the separation of insoluble sulphates, or as also occurs at the separation of native sulphur, e. g. in the case of sphalerite. In the solution itself different processes may run down, exerting an interaction and as the resultant of which the dissolution and oxidation, to a smaller or greater extent, of the different ores can be observed. Sphalerite demonstrates for example how difficultly these processes can be traced. The sphalerite from Herja used for our examinations contains fairly much iron, as pirrhotite. On the action of sulphuric acid  $ZnS + H_2SO_4 = ZnSO_4 + H_2S$  dissolves according to equation simultaneously, however, its pirrhotite content dissolves too according to  $FeS + H_2SO_4 = FeSO_4 + H_2S$  equation. Thus ferrous sulphate forms first which oxidises in the solution to ferric sulphate. The ferric sulphate may exert an action on sphalerite, as well as on the pirrhotite contained in the sphalerite according to equations  $ZnS + Fe_2(SO_4)_3 = ZnSO_4 + 2FeSO_4 + S$ ,  $FeS + Fe_2(SO_4)_3 = 3FeSO_4 + S$ , respectively. However, in addition to these processes the sulphur hydrogen phate and process  $Fe_2(SO_4)_3 + H_2S = H_2SO_4 + 2FeSO_4 + S$  may run down. The formed sulphur may also oxidise further under certain conditions, or separate out as native sulphur. If we still take into consideration that the oxidation of the primarily formed ferrous sulphate can take place according to equations  $12FeSO_4 + 6H_2O + 3O_2 = 4Fe_2(SO_4)_3 + 4Fe(OH)_3$ ,  $4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$ , respectively, as well as that the ferric sulphate can also undergo further changes according to reaction  $Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4$ , than it can, indeed, be seen, why it was stated above that the changes occurring in the free sulphuric acid content cannot alone serve as base for the establishment of the sequel of dissolution; what more, the changes of the bound sulphate content do not either provide a sure base for the establishment of the real sequel of solubility.

Some authors establish the sequel of solubility on the base of the determination of the amount of the sulphur hydrogen formed at the simple dissolving of the ore in unit of time. If only the first reaction would have to be taken into account, e. g. when on the action of sulphuric acid only zinc sulphate and sulphur hydrogen or in the case of pirrhotite ferrous sulphate and sulphur hydrogen form then at the establishment of the sequel of solubility either the decrease of the amount of free sulphuric acid or the increase of the bound sulphate content, as well as the quantity of formed sulphur hydrogen could serve as a base. Actually, however, this is not the case, the primary process is not stable, not final, the changes go on, the first reaction is followed by many others; what more the processes can run down parallel influencing one another as was outlined above. Therefore, at the setting up of the sequel of solubility and of oxidation the changes reflecting the summarization of the processes running down in the



course of the examination, which could also be measured, served as bases. Fig. 2. illustrates the decrease of the free sulphuric acid content between the I. and VI. measurements expressed in  $SO_4$  g/l, as well as the rise detected in the total sulphate content of the solution during the same time also expressed as  $SO_4$  g/l. The figure reflects the tendency to dissolve and oxidise of the different ores and ore-mixtures, respectively, well. The sum of the two changes provides the base for the establishment of the sequel of solubility, whereas the sequel of the oxidation can be established by virtue of the change in the total content.

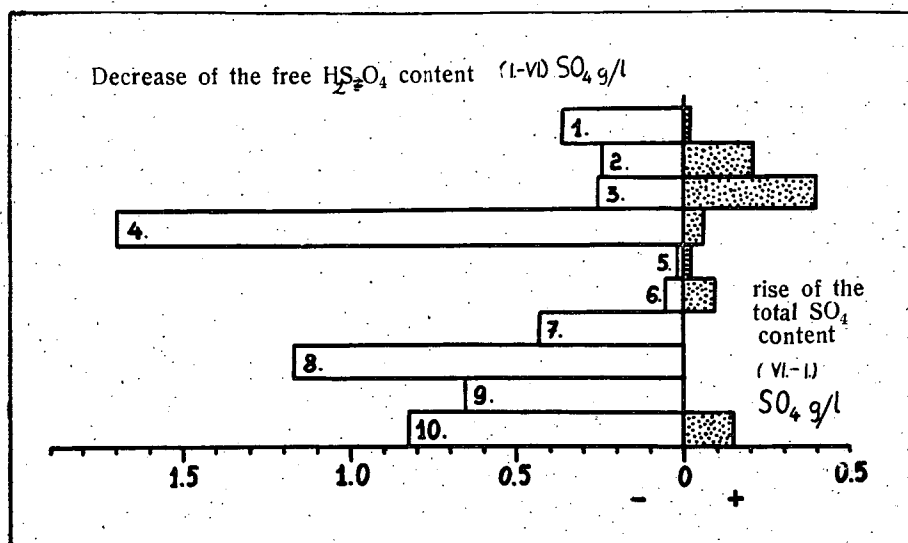


Fig. 2.

The above mentioned establishments served to set up a decreasing solubility sequel for the ores and ore-mixtures, respectively, examined:

„pure ores“:

tetrahedrite, pyrite, sphalerite, galena, chalcopyrite,

ore-mixtures:

8.	10.	9.	7.	6.
galena	tetrahedrite	tetrahedrite	galena	pyrite
chalcopyrite	pyrite	chalcopyrite	chalcopyrite	chalcopyrite
pirrhotite		pirrhotite	sphalerite	sphalerite

It should be mentioned that in the solutions of pure ores in which hydrolytic processes do not occur, the same sequel is obtained on the base of the changes of the pH values.

On the other hand, from the point of view of decreasing oxidation the following sequel can be established.

„pure ores“:

pyrite, sphalerite, tetrahedrite, chalcopyrite, galena,

ore-mixtures:

10.	6.	7.	8.	9.
tetrahedrite	pyrite	in the course of the examination no change could be observed in the total sulphate content of the above mixtures.		
pyrite	chalcopyrite			
	sphalerite			

At the establishment of the sequel reflecting the tendency of oxidation the change occurring in the increase of the total sulphate content of the solution serves as base because the total sulphate content only increases if the sulphur contained in the sulphide ore is oxidised to sulphate. Thus on observing an increase of the total sulphate content, oxidation of the sulphide ore must be taken into account.

According to the literary data the relatively decreasing solubility sequel in aqueous solution is: sphalerite, ..., chalcopyrite, pyrite, galena, ...

*Wells* (5) examined the solubility of several ores in N/20 sulphuric acid. This normality corresponds approximately to the sulphuric acid concentration of the solution with which the experiments were started. He established the following solubility sequel for the ores examined by him: pirrhotite, sphalerite, galena, chalcopyrite, arsenopyrite, marcasite, pyrite. The results of experiments of *Nishihara* (6) in N/8 sulphuric acid given the following sequel: pirrhotite, tetrahedrite, galena, sphalerite, chalcopyrite, arsenopyrite, marcasite, pyrite. It should be mentioned that *Nishihara* carried out similar experiments in ferric sulphate solution obtaining for the above ores the following sequel: pirrhotite, tetrahedrite, galena, arsenopyrite, sphalerite, pyrite, enargite, marcasite, chalcopyrite. *Allen* (7) also performed the same investigation with ferric sulphate solution on fragments taken probably from another deposit and established for their solubility the following sequel: chalcocite, bornite, pyrite, marcasite, covellite, sphalerite, chalcopyrite. The latter two series are only mentioned to demonstrate what an essential role the differences of the reacting solution, as well as the impurities of the various ores, — which is comprehensive in the case of fragments from different deposits — play in the variations which can be observed in the solubility sequel).

In general the sequel set up by us is in good agreement with the experimental results obtained in N/20 sulphuric acid, respectively, of *Wells* and *Nishihara* the only difference being that the pyrite used by us — as contrasted with the literary data — shows a strong tendency to dissolve and oxidise. The significant influence exerted by the size of the granules and the impurities on the solubility and oxidation of the ores should be pointed out. Our pyrite sample was composed of far smaller granules than the others and a very fine ore-powder adhered to them. Thus owing to the quality of the surface and the size of the granules it dissolved and oxidised to a greater

extent than in the case of samples consisting of larger granules. In addition the pyrite contained chalcopyrite impurities, the copper content of the ore was 2,10 per cent corresponding to 6,06 per cent of chalcopyrite which fact plays also a more significant role than the differences in size of the granules. Concerning the effect of the impurities on the solubility it should be noted that according to *Rosenkränzer's* (8) statement sphalerite dissolves more rapidly than galena the more rapidly the greater the iron content of the sphalerite. Our sphalerite being from Herja contains relatively much iron (14,66 per cent) and actually dissolves comparatively more readily than galena. This fact may explain the difference is sequel found by Wells and Nishihara.

It can already now be pointed out that on the base of considerably many quantitative examinations much data are available with respect to the dissolution and oxidation of the different sulphide ores, which data also generally are in good agreement. However, not only the manner how the different pure ores dissolve and oxidise, but rather these conditions, in relation to a certain type and mineral association of a sulphide ore deposit should be dealt with. It could also be seen by virtue of the literary data, as well as our own examinations, that if the results are also mostly in accordance, essential differences can also be detected. For example, both in the present investigations and on the base of the literary data it can be stated that chalcopyrite belongs to the less soluble sulphides. On the other hand, it could actually be experienced that in general the copper ores dissolve to a fairly great extent, which has also been shown by the examinations of the mining waters mentioned above, in which the mean value of the 42 mining water analysis from the sulphide deposits demonstrated that the water contains 11,53 per cent copper expressed in per cents of the dissolved salts, whilst simultaneously the Zn content was 0,53, the Fe 2,41 and the total  $Co + Ni + Cd + Pb$  amounted only to 0.01 per cent. The present examination also proved that the solution circulating through the 300 g. pure chalcopyrite contained at the end of the experiment a total amount of 2,9 mg/100 ml. copper, whereas in the solution circulating through 300 g. pyrite containing 6,06 per cent of chalcopyrite (corresponding to a total amount of 21,81 g. chalcopyrite) 27,6 mg./100 ml. copper could be detected. Namely in addition to the systematical investigation of the behaviour of pure ores — that is to say in so far as natural quite pure ores occur — the investigation of the interaction between the different ores and their environment is very important corresponding to the conditions of the various mining districts, thus rendering it possible to interpret the oxidation and decomposition of the different sulphide ore-deposits. Therefore at the preliminary experiments mixtures were used and our detailed investigations will also be continued according to this trend. Hence, the deviation of the behaviour of our pyrite from the literary data is only an apparent one, because really speaking it was its chalcopyrite impurities which is consequence of its contact with pyrite dissolved to a very great extent. If the pure chalcopyrite was the least

soluble of the examined pure ores and on coming into contact with pyrite yet the chalcopyrite dissolved more readily, then in the sequel of solubility pyrite follows chalcopyrite thus the sequel established by us and that described in the literature is truly in good agreement.

Already *Gottschalk and Buehler* (9) established that in the case of two ores being in complete contact with each other, that having the higher potencial is protected against solution, whereas that having a lower potencial dissolved to a greater extent than if it stands alone. According to *Rechenberg* (10) the potencial of the ores investigated by him are as follows: pyrite 658 mV, chalcopyrite 558 mV and sphalerite 459 mV (he used sphalerite containing 0,13 per cent iron as comparing electrode at the measurements and calculated the results to hydrogen electrode denoting exactly the composition of the solution he used at the measurements as well). Simultaneously he also measured fragments originating from other deposits and obtained the following data: pyrite 540 mV, chalcopyrite 453 mV, sphalerite 181 mV. The latter contained 3,46 per cent iron. In the latter series there were not only shifts in the values, but the potencial sequel of the series also changed. Sphalerite containing more iron showed a smaller potencial and on coming into contact with ores higher up in the sequel dissolved to a greater extent just owing to the potencial difference. This statement was also supported by *Rosenkränzer* and our experimental results yielded the same data concerning sphalerite.

It can be seen therefore that small deviations in the impurities result in significantly different solubility conditions. This fact supports our assumption that though it is necessary to investigate the behaviour of the various ores, however, the greatest stress must be put on the study of the conditions of interaction, and of the oxidation and solubility of the mineral associations dominating and characterising a mining district.

Thus on the base of the work of the author mentioned above the question arises if it is suitable to speak of the sequel of potencial of ores in general, as also according to the authors (10) establishment mechanical or isomorphous impurities, or differences in the chemical composition, can cause essential deviations. If samples from the same ore deposit are investigated no significant differences can be detected in the potencial series on carrying out the examinations in solutions of either acid (pH 4) or basic (pH 9) character; however, essential deviations in value, and what more in the sequel could be observed when ores originating from other mining districts were similarly investigated. On the other hand, the deviation of the sequel results in the ores behaving differently from the point of view of dissolution.

On the dissolution ferrous sulphate forms primarily which may oxidized to ferric sulphate, and this in turn on the action of sulphur hydrogen, arising in the course of the solution, or through that of the fresh sulphides can again be converted to ferrous sulphate. Considering that it was in any way contemplated to determine the iron contained in the solutions, simultaneously the amount of ferrous and ferric iron, respectively, was also estimated.

Table 4.

*The change of the content of ferrous (a), ferric (b), as well as the total iron (c) contained in the solutions:*  
Fe mg/100 ml

	III.			IV.			VII.		
	a	b	c	a	b	c	a	b	c
1.	0.48	7.42	7.90	1.90	10.4	12.3	3.8	23.3	27.1
2.	0.18	8.42	8.60	0.7	11.9	12.6	0.5	25.3	25.8
3.	0.20	4.7	4.9	1.70	3.2	4.9	2.4	37.2	39.6
4.	5.72	4.08	9.80	11.6	0	11.6	65.6	13.8	79.4
5.	0.10	3.3	3.4	1.2	7.3	8.5	0.7	1.01	10.8
6.	0.1	4.7	4.8	1.05	7.3	8.35	1.05	18.05	19.1
7.	0.1	9.7	9.8	2.05	14.75	16.8	11.0	39.4	50.4
8.	0.25	10.6	10.85	12.40	0	12.40	28.05	72	100.5
9.	0.52	9.5	10.02	12.10	0	12.10	27.5	51.9	79.4
10.	0.35	8.93	9.28	3.0	6.10	9.10	0.9	59.4	60.3

The change of the manganese content of the solutions was investigated. If it was also not yet possible to establish a correlation between the change of the ferrous and ferric content of the solutions and the dissolution and oxidation of the ores, yet the comparison of the changes of the manganese and iron content of the solutions showed clearly that the separation of the adjacent iron and manganese in the ores takes place in the same manner during the decomposition as in the case of the sulphide ores, and in that of the carbonates, or silicates. The manganese dissolves earlier than the iron, it is maintained over a longer period in solution and is transported in this state, whereas the iron dissolves later and separates out first, thus the originally

adjacently occurring iron and manganese are also separated spatially and in time in the course of the secondary cycle.

Table 5.  
*The change of the manganese content of the solutions.*  
Mn mg/100 ml.

	I.	II.	III.	V.	VI.	VII.
1.		1.261	1.581	2.171	2.363	2.700
2.	0.312		0.642	0.667		1.000
3.	0				0	0
4.	0.104		1.167	3.544	4.135	4.500
5.				00.38	00.44	0.160
6.	0.147		0.255	0.315		0.710
7.	0.295		0.529	0.538	0.608	0.900
8.	0.139	0.243	0.337	0.340		0.760
9.	0.512		1.372	2.171	2.293	3.000
10.	0.326		1.160	2.328	2.703	3.300

On contemplating the change in time of the manganese and iron content of the solution it can immediately be seen that in general the greater part of the change of the manganese content, estimated between the first and last measurements, fell into the first part of the series of experiments, while in the case of the iron content it rather fell into the last period.

On considering the curves showing the change in time of the manganese content the strong resemblance between curves No. 4. and 10. and No. 2. and 6., 7., 8. is striking. It is particularly pronounced in the latter curves. This similarity is due to the fact of the manganese content of the solutions of the mentioned ores and ore-mixtures, respectively, changing in the same proportion, if the differences of order of magnitude are not taken into consideration.

The change of the manganese content of solution No. 10. is very similar to that observed in solution No. 4. Thus the conclusion can be drawn that the manganese content of solution No. 10. was furnished by the dissolution of tetrahedrite and that tetrahedrite dissolved in the first place in the ore-mixtures mentioned above. On the other hand, the ratio of the change in the solutions of the ore-mixtures No. 6., 7., 8. corresponds to that observed in the solution of pure sphalerite. Thus it can also be assumed that the manganese content of these solutions is due to the dissolution of the sphalerite contained in the ore-mixtures, the more so since mixtures. No. 6. contained in addition to sphalerite also pyrite — not containing any manganese — and chalcopyrite, which contained very minimal amount of manganese, however, at the end of the series of experiments chalcopyrite did not show any signs of dissolution its surface was quite intact.

Sample No. 7. contained besides sphalerite also chalcopyrite and galena, the latter contained a considerable amount of sphalerite as

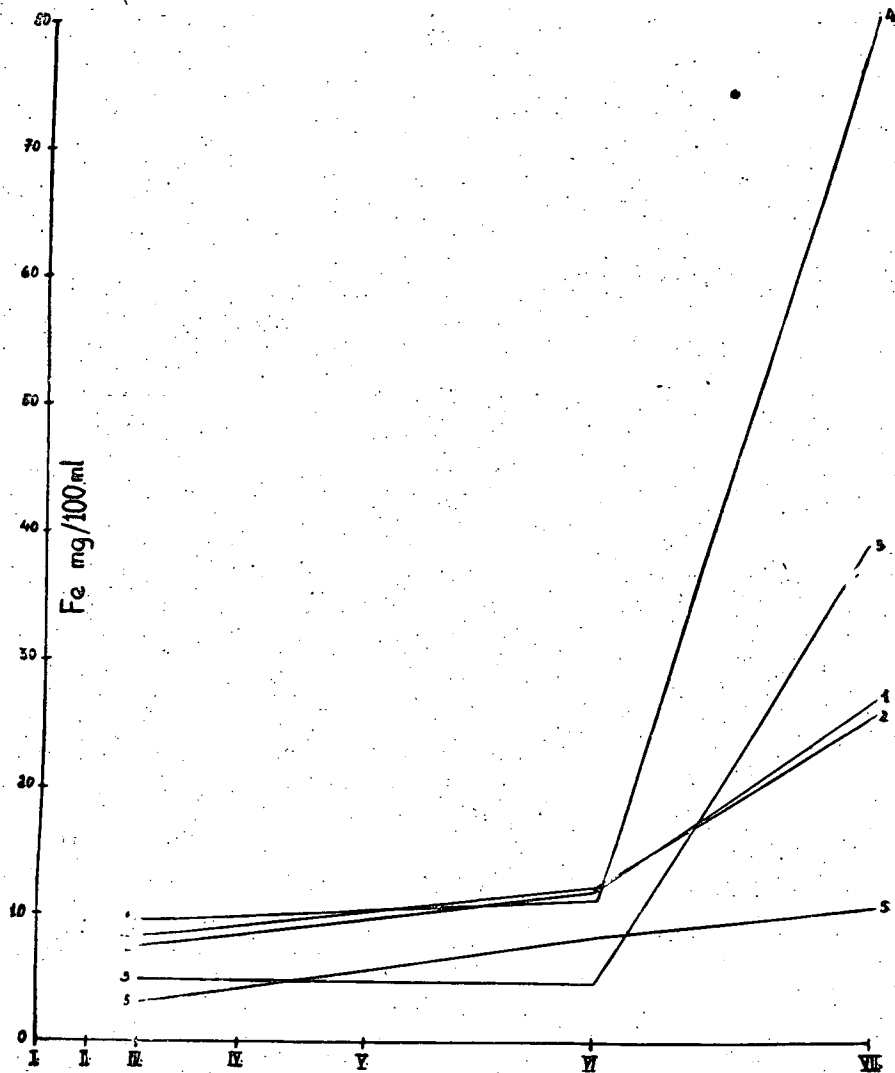


Fig. 3.

*The change of the iron content of solutions No. 1—5.*

mechanical impurities. The solution of pure galena contained relatively amount of manganese, which exceeded that contained in the solution of pure sphalerite. In this case on the other hand, the manganese content of solution No. 7. does not increase, not even exceeding that contained in the solution of pure sphalerite, the charge being quite identical with that observed in the case of sphalerite. Thus it must also be established that owing to the mutual contact galena was pre-

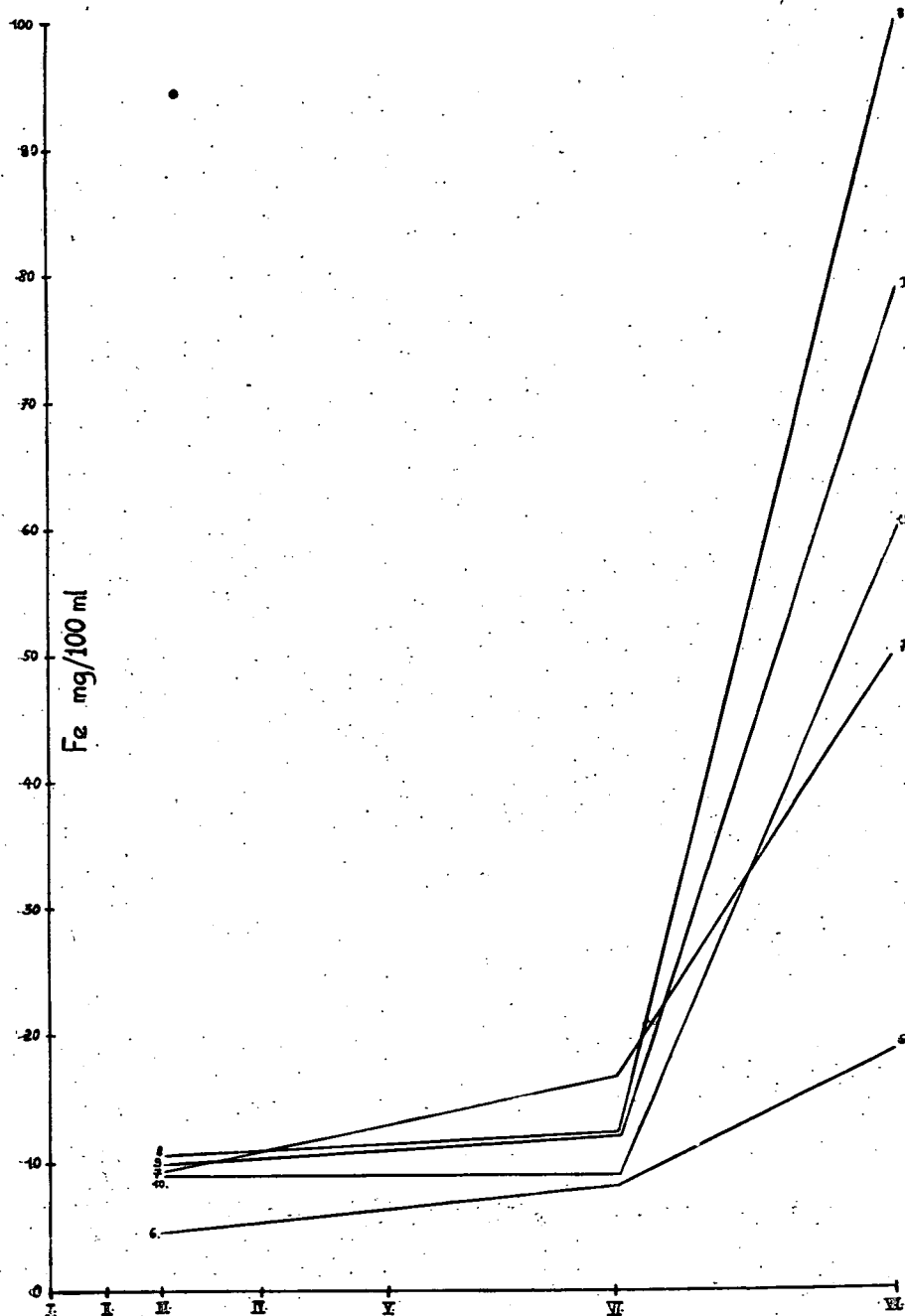


Fig. 4.

The change of the iron content of solutions No. 6—10.



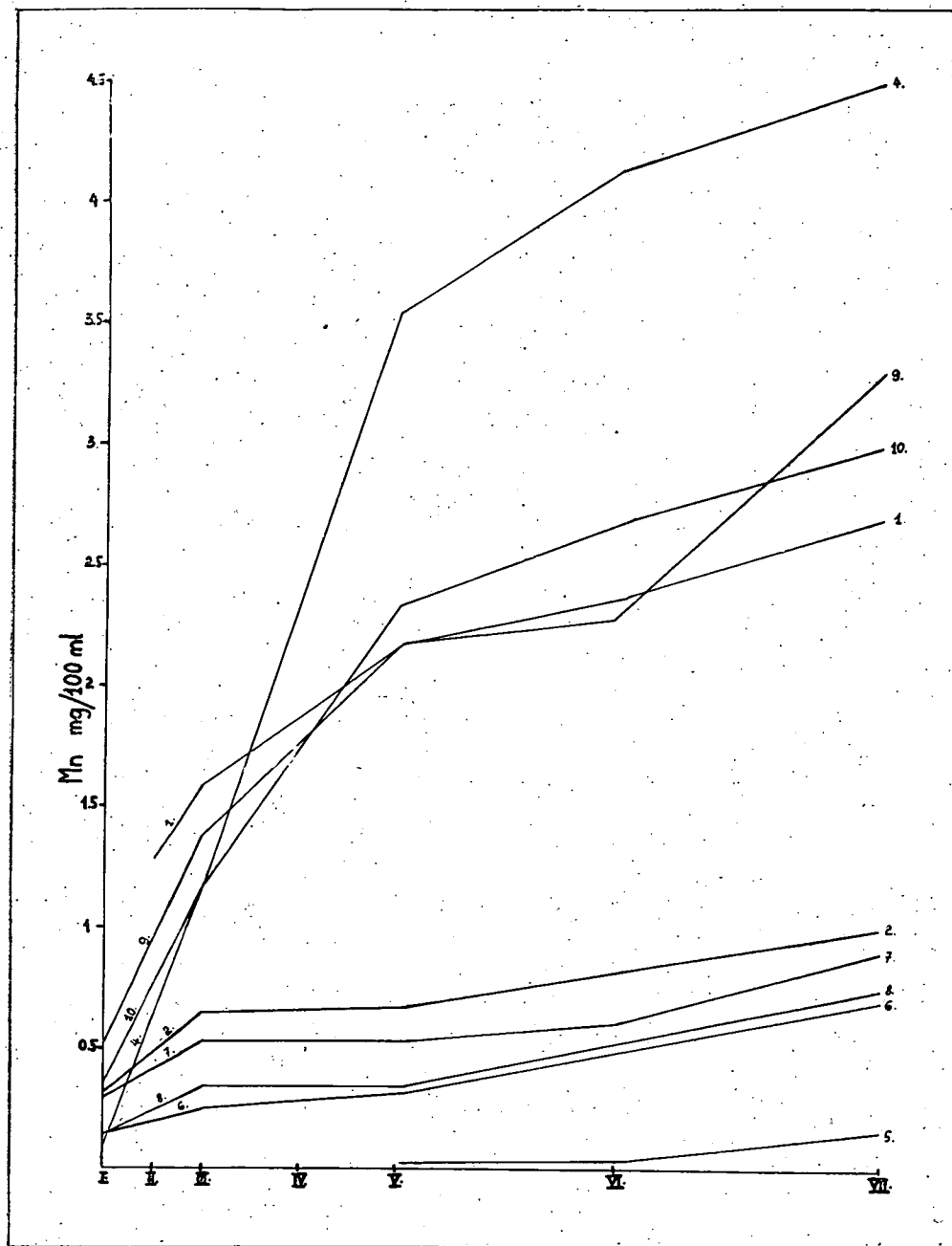


Fig. 5.

The change of the manganese content of solutions.

tested against dissolution and hence rather the sphalerite dissolved furnishing the manganese content of the solution.

At the end of the examination chalcopyrite was also quite intact. The comparatively high Zn content of the solution also points to the vigorous dissolution of sphalerite, at the last measurement it was 21.9 mg Zn/100 ml.

Solution No. 8. did not contain sphalerite any more, merely galena containing as mechanically impurities sphalerite, the latter being in close contact with galena furnished the manganese content of the solution.

The Fe, Mn, Zn, Cu content of the solutions were also determined from the last sampling.

Table 6.

*The Fe, Mn, Zn, Cu content of the solutions (mg/100 ml).*

		Fe	Mn	Zn	Cu
1.	Galena	21.7	2.7	20.2	—
2.	Sphalerite	25.8	1.0	36.9	in trace
3.	Pyrite	39.6	—	—	27.6
4.	Tetrahedrite	79.4	4.5	—	7.1
5.	Chalcopyrite	10.8	0.16	—	2.9
6.	Pyrite Chalcopyrite Sphalerite	19.1	0.71	1.6	11.6
7.	Galena Chalcopyrite Sphalerite	50.4	0.90	21.9	0.5
8.	Galena Chalcopyrite Pirrhote	100.5	0.76	in trace	0.8
9.	Tetrahedrite Chalcopyrite Pirrhote	79.4	3.00	—	4.2
10.	Tetrahedrite Pyrite	60.3	3.30	—	16.0

As can be seen though galena contained sphalerites as mechanical impurity, the amount of this sphalerite being therefore manifold less than that of the pure sphalerite of sample No. 2., yet the amount of zinc is more in the solution of galena than half of the zinc quantity of the solution of the pure sphalerite, i. e. when the sphalerite is in close contact with galena it undergoes a far more vigorous dissolution

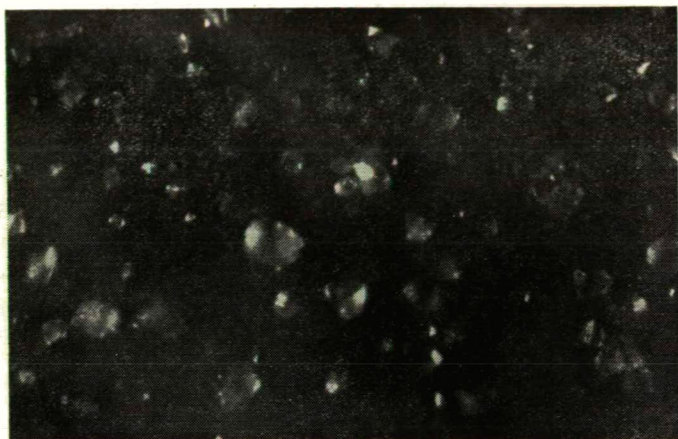
than alone. The iron content pro liter in the solution of pure galena corresponds to 0,426 g.  $FeS$ , its zinc content to 0,301 g.  $ZnS$ , whereas the iron content of the solution of pure sphalerite corresponds pro liter to 0,406 g.  $FeS$ , its zinc content to 0,549 g.  $ZnS$ .

The significant action exerted by direct and close contact of the ores on the dissolution could be also observed in the case of the other ores. The copper content of the quite pure solution of chalcopyrite corresponds to 0,0836 g.  $CuFeS_2$  pro liter, while the copper content of the solution of pyrite (No. 3.) contained 6,06 per cent chalcopyrite as mechanical impurity corresponding to 0,7969 g.  $CuFeS_2$  pro liter, i. e. in the case of a close contact between pyrite and chalcopyrite, the chalcopyrite decomposes to a great extent. Mixtures No. 6., 7., 8., 9. also contain chalcopyrite, however, the chalcopyrite granules contained in them remained quite fresh. The chalcopyrite content of the solution of these mixtures may derive from the other minerals of the mixtures, in these mixtures chalcopyrite was protected against solution having a higher potencial than the other minerals. Although in mixture No. 6. the chalcopyrite granules added to the mixture remained quite fresh the copper content of the solution was after all relatively high, 11,6 mg/100 ml. However, the mixture also contained pyrite containing as mentioned above 6,05 per cent of chalcopyrite, thus the contact between the pyrite and chalcopyrite, was very close. This fact shows that in addition to the contact brought about by the mining-water — essentially an electrolyte solution — the role of a complete contact like that existing between an ore and its mechanical or isomorphous impurities, or one as can also be found in the case of an ore lode, is far more important. This is illustrated by the zinc content of the solution of mixtures No. 6. and 7. These mixtures contain sphalerite in the same proportion, yet solution No. 6. contains only 1,6 mg/100 ml Zn and the copper content in turn amounts to 11,6 mg/100 ml, whereas solution No. 7. already contains 21,9 mg/100 ml Zn, its copper content in turn only being 0,5 mg/100 ml. Though in mixture 6. the potencial of the sphalerite is lower than that of the other ores, thus it ought to dissolve to a far greater extent, yet its contact with the other ores is by far not so complete than that between the pyrite and chalcopyrite contained in the former, if also only in a minimal amount as mechanical impurity. Thus in the first place the chalcopyrite dissolved furnishing the copper content of the solution. The pure chalcopyrite added to the mixture did not show any dissolution. On the other hand, mixture No. 7. also contained beside pure sphalerite galena impurified with sphalerite, thus the vigorous dissolution of sphalerite is comprehensive.

On concluding the first part of the series of experiments the minerals exposed to the action of the sickering solution were also examined, as to what changes could be observed on their surfaces and what kind of secondary minerals had formed.

The most conspicuous change could be observed in the case of galena and sphalerite. The surface of all the galena fragments are incrustated with a layer of cerussite. Either tiny crystals form a

uniform crystalline crust on the surface of the ore, in which case the shapes of the single crystals cannot even be detected under high magnification, only single platelets glistening up, or tiny crystals, 0.02—0.1 mm in size, transparent, mostly tabular, according to (010), are deposited directly on the galena, or on the crystalline crust mentioned above, respectively. (Fig. 6.)



*Fig. 6. Crystals of cerussite on galena.*

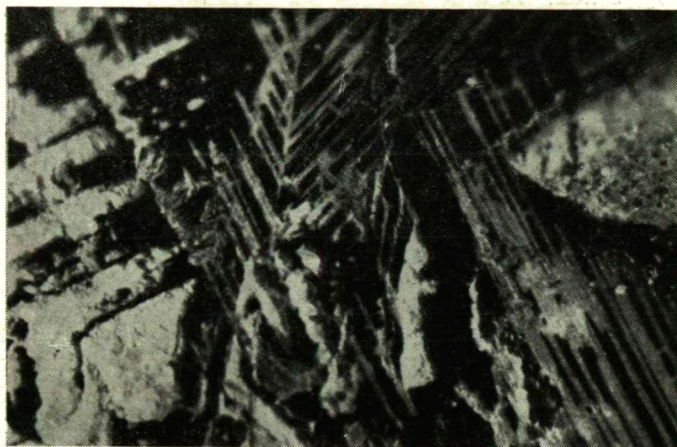
The tabular crystals on the single hexahedron surface of galena are all oriented, the larger of them formed through the oriented intergrowth of numerous tiny crystals, the glistening of their identical platelets occurs simultaneously. These cleavage surfaces of the galena are oriented in the direction of the sickening solution, the growing cerussite crystals developed in the direction of the slightest resistance with brightly glimmering faces of the first and third order prisms. On another surface of the same galena cleavage hexahedron, which surface is situated in the shadow of the flow the solution, the crystals are thicker tabular, each crystal forms an individual, there is no oriented intergrowth and they are placed arbitrarily. Thus the habit of the crystals separating out from the following solutions is influenced to a great extent by the fact of them developing on a surface situated in the direction of the flow, or on a plane in the shadow. It is deemed of interest to carry out further investigations concerning the differences observed on the habit of the cerussite crystals which can be attributed to the influence of the flowing solution.

On some of the galena samples a few cerussite crystals could be detected, on which the faces (100) and (010) were developed in equilibrium, the form (110) could be seen as narrow bands, the crystal was terminated by the platelets of the unit pyramide. On dissolving the tiny cerussite crystals, their negative can be seen impressed in the galena.



In the fine fissures of certain galena samples antimonite needles could be observed. On these samples the fanlike, sheathslike crystal groups of valentinite, showing a pearly luster, may be detected.

The cleavage surfaces of black sphalerite crystals from Herja containing some galena and pyrite as mechanical impurities are incrustated with a thin bluish, or thicker yellowish pearly lustreous film (Fig. 7.).



*Fig. 7. Separation of sulphur along the twin lamellae of sphalerite.*

The film is formed of sulphur. Its separation always starts along the twin lamellae and when the separation advances the whole surface becomes coated. The initial separation of sulphur along the twin lamellae shows very well that the sphalerite fragments are polysynthetic twin crystals.

On removing the sulphur coating the silky glimmering etched surface of the attacked ore is well visible. On the thin sulphur film the tiny unit pyramidal crystals of the sulphur 0.01—0.02 mm. in size showing a diamond luster, can be found, which frequently exhibit parallel intergrowths (Fig. 8.).

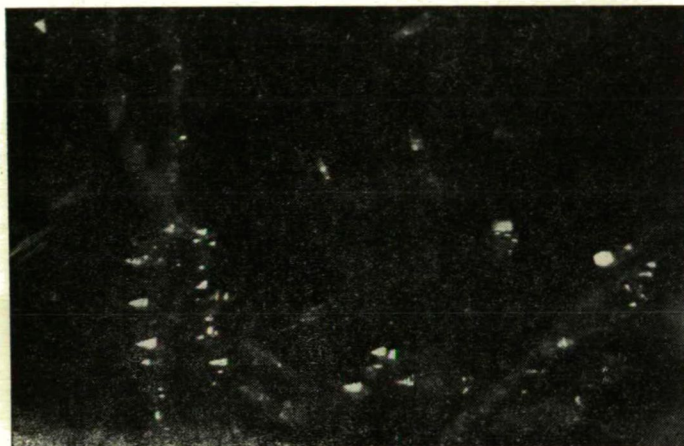
It is interesting to note that the sulphur crystals always show an identical orientation, axis *c* is parallel to the direction of the flowing solution.

On the samples of sphalerite the thin needles of gypsum elongated according to axis *c* can be sometimes observed.

The galena crystals contained as mechanical inclusions in sphalerite are also covered with cerussite like the pure galena samples mentioned above. On the pyrite crystals contained as mechanical inclusions in sphalerite as well, a coating could never be detected, however, the crystal faces were slightly attacked. Where the three ores — sphalerite, galena, pyrite — are in contact the sphalerite is coated with a thin sulphur film, galena with a cerussite crust, whereas pyrite glimmers with a silky luster.

The pyrite granules are covered on some points with iron hydroxide, on others there were no visible changes.

The surface on chalcopyrite is coated with a very thin dark indigo-blue film which already disappears on gentle rubbing. It consists most likely of covellite. On the places where the glass tube was surrounded by a tin ring, thus where the chalcopyrite contained in the tube was not exposed to light the colour of the coating is far darker, nearly black.



*Fig. 8. Oriented crystals of sulphur on sphalerite.*

On the fragments of tetrahedrite a lighter coating, less pronounced than that of chalcopyrite, could be observed, however, the coating appeared only in patches. The siderite granules contained in tetrahedrite as mechanical inclusions dissolved to a great extent, on their surface and along their cleavage direction iron hydroxide separated out staining the siderite granules rust-coloured.

The minerals of the ore combinations showed in general the same changes as the more or less pure ores, having been exposed to the action of the mining-water. Chalcopyrite is an exception it remains in every mixture quite fresh. On the surface of the sphalerite contained in the mixtures the sulphur separation is not so great. The tetrahedrite granules are also irised tarnished in ore combinations. In the mixtures the surface of the pyrrhotite granules is everywhere covered with iron hydroxide.

On the minerals used for the examinations in the course of the laboratory experiments the following secondary minerals form: cerussite, native sulphur, valentinite, gypsum, covellite,  $Fe(OH)_2$ .

In the course of further examinations the solubility and oxidation conditions of an ore combination corresponding to the mineral association of Reesk will be investigated. Furthermore, the influence of the manganese- and copper sulphate content of the solutions on the oxidation of their ferrous sulphate content will also be examined.

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