

DATA ON THE OXIDATION OF SULPHIDE-ORE DEPOSITES

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Our investigations published last year dealt in general with the dissolution and oxidation — resulting from the action of sulphuric acid solutions — of some significant sulphide ores such as galena, sphalerite, pyrite, tetrahedrite, as well as ore mixtures consisting of these ores and their mixtures with pyrrhotite. In the course of the examinations the change in the free sulphuric acid and total sulphate content, the change in the pH and conductivity, as well as that of the metal content were measured. On the basis of these measurements a distinct correlation could be established between the change relating to the factors mentioned above and those concerning the dissolution and oxidation of the different ores and ore mixtures. It should be established that the environment exerts a very strong influence on the dissolution of the various ores, as well as the difference in potential existing between the respective ore and other neighbouring ore granules. The extent of the change is well reflected by the aforementioned changes the measuring of which can be effected in a relatively short time.

In the following the continuation of our work of last year in the sense described then is contemplated i. e. that the study of the dissolution and oxidation conditions of the ore debris corresponding to the mineral association characterising an individual mining district is the chief purpose, notwithstanding that the dissolution conditions in general must also be dealt with, as the dissolution and oxidation conditions of the different ores are strongly influenced by their environment and impurities, more precisely they are determined by them. For this reason the mineral association of Recsk was investigated first. Simultaneously we attempted to establish to what an extent the copper sulphate and ferric sulphate content of the solutions sickering over the ores influences their dissolution. Selected „pure” enargite, as well as a mixture of enargite-pyrite was treated with a solution of 0,05 N sulphuric acid containing copper and ferric sulphate respectively, as well as with one of 0,05 N sulphuric acid and similarly to last year the changes occurring in the solution were examined. A separate sample was selected to observe the dissolution conditions of the pyrite of Recsk, it was treated with a pure sulphuric acid solution of the concentration mentioned above. The apparatus described in our previous communication was used and the course of the examination was identical too.

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The tests were as follows:

Composition of the test:

1. Pure selected enargite
2. Pure selected enargite
3. Pure selected enargite
4. Ore mixture (enargite-pyrite)
5. Ore mixture (enargite-pyrite)
6. Ore mixture (enargite-pyrite)
7. Pure selected pyrite

Composition of the circulating solution:

- about 0,05 N sulphuric acid.
 about 0,05 N sulphuric acid + ferric sulphate. Iron content of the starting solution 0,2236 g/l Fe.
 about 0,05 N sulphuric acid + copper sulphate. Copper content of the starting solution 0,2847 g/l Cu.
 Like solution 1.
 Like solution 2. Iron content of the starting solution 0,2348 g/l Fe.
 Like solution 3. Copper content of starting solution 0,2782 g/l Cu.
 Like solution 1.

The change of the amounts of free sulphuric acid, total sulphate, iron, copper and arsenic contained in the solutions was examined. The results are illustrated in the following tables: (In the period between the taking of the first and the last sample the same 5 liters sicker twelve times over the ores, the amount merely decreasing through the sampling.)

Table 1.

The change of total sulphate (a), free sulphuric acid (b) and bound sulphate (c) contained in the solutions in SO_4 g/l :

Solution	at the beginning	at the end	change in the course
	of the examination		
1. a	2,158	2,286	+ 0,128
	b	2,158	- 0,054
	c	0,000	0,182
2.	3,090	3,185	+ 0,095
	2,518	1,948	- 0,570
	0,572	1,237	+ 0,665
3.	2,678	2,891	+ 0,213
	2,248	1,819	- 0,429
	0,430	1,072	+ 0,642
4.	1,933	2,396	+ 0,463
	1,933	1,952	+ 0,019
	0,000	0,444	+ 0,444
5.	3,010	3,294	+ 0,284
	2,405	1,729	- 0,676
	0,605	1,565	+ 0,960
6.	2,668	2,942	+ 0,274
	2,248	1,886	- 0,362
	0,420	1,056	+ 0,636
7.	2,068	2,299	+ 0,231
	2,068	1,862	- 0,206
	0,000	0,437	+ 0,437

Table 2.
The change of the iron- copper- and arsenic content
of the solutions in g/l:

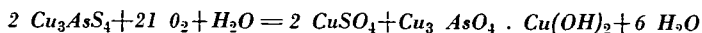
Solution		at the beginning	at the end	change in the course
		of the examination		
1.	Fe	0	0,0091	0,0091
	Cu	0	0,0198	0,0198
	As	0	0 0035	0,0035
2.	Fe	0,2236	0 2348	0,0112
	Cu	0	0,0039	0,0039
	As	0	0,0020	0,0020
3.	Fe	0	0,0548	0,0548
	Cu	0,2847	0,3089	0 0242
	As	0	0 0100	0 0100
4.	Fe	0	0,0891	0,0891
	Cu	0	0,0094	0,0094
	As	0	0 0025	0,0025
5.	Fe	0 2348	0,2815	0,0467
	Cu	0	0,0145	0,0145
	As	0	0,0030	0,0030
6.	Fe	0	0,0822	0,0822
	Cu	0,2782	0,3242	0,0460
	As	0	0,0045	0 0045
7.	Fe	0	0,0572	0,0572
	Cu	0	0,0090	0,0090
	As	0	0,0015	0,0015

In the course of the investigations carried out in 1952 in most cases merely the free sulphuric acid content diminished, however, the total sulphate content remained unchanged. On the other hand, in the solutions circulating over the pyrite-enargite mixture the total sulphate content increased significantly, to a greater extent than in the solutions circulating over the pure pyrite or pure enargite. Indicating that in cases when the pyrite and enargite are in contact, the oxidation is more intense than in the case of pure ores in spite of the difference in potential being slight between the two ores. The pyrite-enargite mixture underwent the most intensive oxidation in pure N sulphuric acid (0,05), inasmuch as not only the total sulphate content increased to the greatest extent, but even the amount of the free sulphuric acid contained in the solution increased.

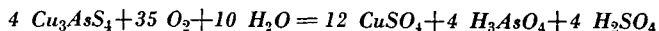
Pyrite dissolves and oxidizes to a greater extent in a solution of pure sulphuric acid than enargite. Based on the results of the previous and present investigations the following sequel can be established according to the decrease in solubility: tetrahedrite, sphalerite, galena, pyrite, enargite, chalcopyrite.

These results are in good agreement with the results reported by Nishihara regarding his investigations carried out in ferric sulphateous solutions.

It can be assumed that the oxidation of enargite takes place according to the following equation:



Accordingly basic copper arsenates forms. However, they decompose on the action of sulphuric acid and if the latter is not bound in some way, arsenates do not form, but the enargite containing copper dissolves totally and in addition to copper sulphate and free sulphuric acid $\text{H}_3 \text{AsO}_4$ also forms. Thus in this case the oxidation of enargite can be represented as follows:



This explains the increase of the amount of the total sulphate and free sulphuric acid contained in the pure sulphuric acid solution circulating over the pyrite-enargite mixture. The change of the total sulphate content expresses the extent of the oxidation as the total sulphate content of the solution only increases if the sulphide contained in the ores is oxidized to sulphate.

The change of order of magnitude of the arsenic content is nearly identical to that of the copper content. The amount of copper and arsenic contained in the solutions shows the greatest increase both in ores and ore mixtures if they are exposed to the action of solutions containing copper sulphate. In solutions containing copper sulphate the change of the iron content is also more significant than in solutions containing ferric sulphate.

Our present investigations support also the results obtained in 1952, inasmuch as in the case of the mixtures — although there is a small potential difference between pyrite and enargite — the increase of the total sulphate content (the oxidation of the ore) exceeds appreciably the change of the total sulphate amount measured in the solutions circulating over the pure enargites.

In pure sulphuric acid solutions the pyrite decomposition sets in initially as indicated by the high iron content observed in solution No. 4, as well as by the fact that the iron content of the pure, selected solutions circulating over the enargites, containing at the most quite slight pyrite impurities also increases considerably in a relatively short time. On the action of the evolved ferric sulphate and sulphuric acid in the presence of air the oxidation of the enargite starts and becomes always more intensive as the concentration of the copper sulphate and sulphuric acid increases, and if the sulphuric acid forming in the course of the decomposition is not bound in some way, the enargite is oxidized to copper sulphate and arsenic acid under formation of sulphuric acid. The experiments show that indeed copper sulphate exerts a more intensive action than ferric sulphate. If the sulphuric acid concentration diminishes significantly it paves the way for the formation of different copper arsenates. Taking the mineral association of Reesk into consideration it seems probable that the oxidation takes place as described above.

The results reported in our previous paper point to the fact that for the interpretation of the dissolution and oxidation conditions of the different ores and ore mixtures (their combination corresponding to the different mineral associations) the changes of the sulphuric acid and sulphate content, as well as those of the pH, conductivity and those of the amount of the contained metal, do not offer a suitable explanation, hence the observed phenomena cannot be solely due to the changes described above. For instance there

is no explanation for the change of the ferrous-ferric ratio, as well as for the fact that e. g. not the slightest iron hydroxide separation could be detected in the solution circulating on the tetrahedrite the pH of which was 2,40 and its free sulphuric acid content 0,78 g H_2SO_4/l ; whereas in a solution circulating on an ore mixture of galena-chalcopyrite-pyrrhotite the pH of which was 2,00, containing 1,760 g H_2SO_4/l , or in a solution of pH 2,20 containing 1,331 g H_2SO_4/l of free sulphuric acid circulating over a tetrahedrite-pyrite mixture, an intensive iron hydroxide separation could be observed.

The redoxypotential on the other hand, also provides an adequate explanation for these phenomena. Goldschmidt was the first to use the term oxidation potential in geochemistry, recently Scserbina, Mason, Chapman, and Schweitzer also use it. The dissolution, transport and separation respectively, of elements occurring in different oxidation forms are greatly influenced by the oxidation potential of the environment, i. e. the latter determines it.

The potential of a system is the more negative the higher the concentration of the ions of lower valency compared with those of higher valency and on the other hand, the more negative the normal potential, the more vigorously the system reduces, whereas the more positive the potential of a system the more vigorously it oxidizes in the case of identical concentrations. Hence every system exerts a reducing influence on the systems having a more positive redoxypotential and vice versa.

In the course of our previous investigations we observed that a tetrahedrite solution mainly contained iron as ferrous iron and that in the course of the circulation the ferrous content of the solution increased intensely, or that e. g. in a solution of tetrahedrite-chalcopyrite-pyrrhotite the ferrous content also showed a rise, whereas in other cases as for example a solution of galena or sphalerite or even in that of pyrite the increase of the ferrous iron content was very slight even decreasing in some places in spite of the fact that in the course of the dissolution it dissolved first as ferrous iron. Thus in the case of the latter ores the oxidation was more intense than in that of the former ones. In the course of the experiment the quantity of the dissolved metals was also determined. As among these metals in the case of iron, copper and manganese the valences vary, it is obvious that in the first place the action exerted by copper and manganese on the change of the ferrous-ferric ratio had to be examined.

The potential of $Fe^{+2} = Fe^{+3} + e$ is 0,77 V, that of $Mn^{+2} = Mn^{+3} + e$ 1,57 V and that of $Cu^{+1} = Cu^{+2} + e$ 0,18 V. The values represent the normal oxidation potential, i. e. when the oxidized and reduced forms are present in equal concentration. This value is influenced by the change of concentration. For instance the normal potential of Fe^{+2}/Fe^{+3} is 0,77, if the Fe^{+3}/Fe^{+2} ratio is 100/1 the oxidation potential is 0,89 V, if on the other hand the Fe^{+3}/Fe^{+2} ratio is 1/100 then it will be 0,65 V.

In the range of a certain pH the latter does not influence the oxidation potential. Thus for instance the oxidation potential of Mn^{+2}/Mn^{+3} remains constant till pH 4, in an acid medium the oxidation potential of Fe^{+2}/Fe^{+3} is 0,77 V, as the pH increases and attains a certain value, approximately at pH 2—3, the oxidation potential suddenly decreases and the separation of the ferric hydroxide sets in. We also observed that at the decomposition of sulphide ores — like at that of the silicates and carbonates — the iron and manganese occurring primarily associated separate in the course of the decom-

position the iron separating out first in the form of hydroxide. This phenomenon can also be accounted for by the variations of the oxidation potentials.

Of the three systems involved the $\text{Cu}^{+1}/\text{Cu}^{+2}$ system has the lowest, the $\text{Fe}^{+2}/\text{Fe}^{+3}$ the mean, and the $\text{Mn}^{+2}/\text{Mn}^{+3}$ the highest potential. The influence exerted by copper sulphate and manganese sulphate on the oxidation of ferrous iron to ferric iron in a 0,05 N sulphuric acid solution was examined, as well as the rate of the ferrous oxidation if copper sulphate and manganese sulphate are simultaneously present. Hence the change of the ferrous content was systematically measured in sulphuric acid solutions the composition of which corresponded to that described above.

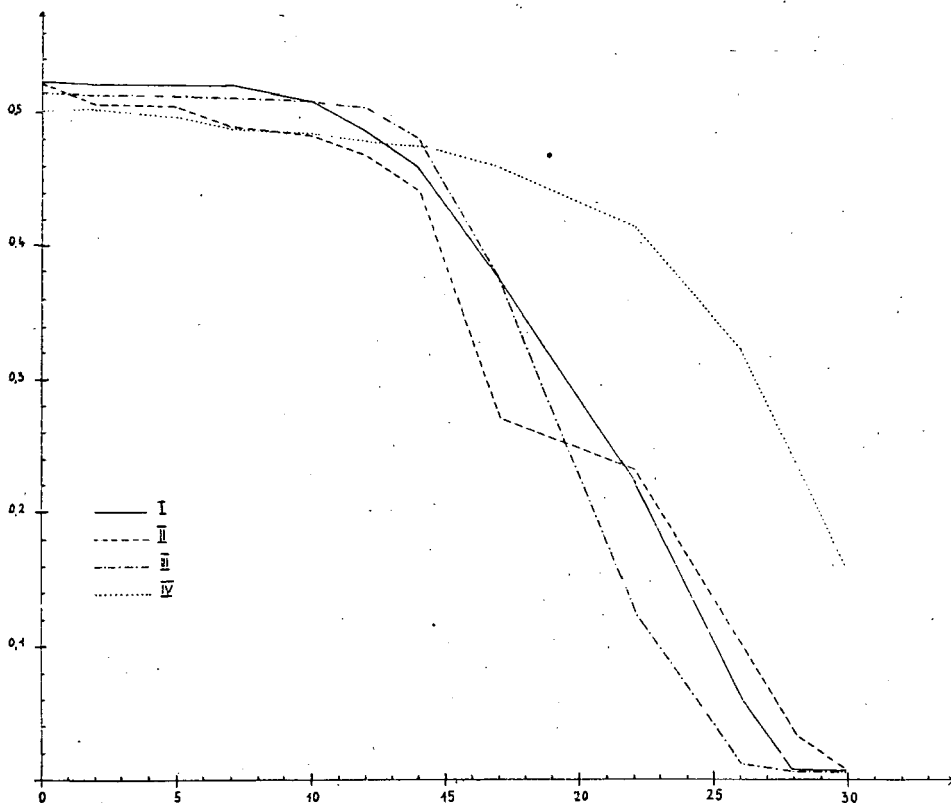
Solution No. I. contained only ferrous sulphate, the iron content of the solution at the start was 0,522 g Fe/l. Solution No. II. contained the same amount of iron and 0,273 g/l copper as copper sulphate. Solution No. III. contained 0,514 g/l ferrous iron and 0,184 g/l manganese as manganese sulphate. Finally the ferrous iron content of the solution No. IV. was 0,502 g/l and contained the same quantity of copper and manganese as in the case of solutions III., IV. respectively. The sulphuric acid concentration of the solutions was about 0,05 N.

Table 3.
The change of the ferrous iron content in g/l:

The data according to the days after the examinations were started	I	II	III	IV
	solutions			
0	0,522	0,522	0,514	0,502
2	0,520	0,506	0,512	0,502
5	0,520	0,504	0,512	0,496
7	0,520	0,490	0,510	0,488
10	0,508	0,482	0,508	0,484
12	0,486	0,468	0,504	0,478
14	0,458	0,442	0,480	0,474
17	0,374	0,272	0,376	0,458
22	0,224	0,232	0,126	0,414
26	0,060	0,100	0,012	0,322
28	0,006	0,034	0,006	0,240
30	0,006	0,006	0,006	0,164
60	0,003	0,006	0,003	0,006

On the basis of the above considerations, as was anticipated, the rate of the oxidation of ferrous iron was slower in copper sulphateous solution and more rapid in manganese sulphateous solutions, as compared with the oxidation of the ferrous iron contained in pure sulphuric acid ferrous sulphate. On the other hand, in the solution where the starting solution contained manganese sulphate and copper sulphate simultaneously the oxidation-reduction processes run down in the first place between the lowest and highest potential system. Thus owing to the action of the oxidation potential the simultaneous presence of manganese and copper retards the oxidation of ferrous iron. This assumption, as well as the significance of the influence of the oxidation potential on the different processes is supported by the establishment made in the course of our previous examinations that the ferrous iron content of the solutions circulating over the tetrahedrite ore debris — containing at the end of the experiment-series 0,045 g/l — manganese and 0,071

g/l copper was permanently dominating, the amount of the ferrous content exceeding manifold that of ferric iron.



On the other hand, in the case of sphalerite or galena the solutions circulating over them contained only manganese, but no copper, thus the manganese accelerated the oxidation of the ferrous iron and ferric iron dominated in the solutions.

It is contemplated to investigate the significance and role of the oxidation potential under conditions in which a solution is also in contact with a solid phase.

ОКИСЛЕНИЕ ПДАСТОВ СЕРНИСТЫХ РУД.

— ШАНДОР КОХ И ЮЛИЙ ГРАССЕЛЛИ —

Продолжая прошлогодние исследования по растворению и окислению рудной мелочи-чистого пирита, чистого энаргита или смеси пирита-энаргита, соответствующему составу минерального агрегата месторождения Речка, устанавливалось, что прежде начинается разложение пирита, а потом, по воздействию образованного сульфата железа и серной кислоты, начинается и окисление энаргита. Последний процесс становится всё сильнее по мере действия возрастающей концентрации сульфата меди и серной кислоты и если образованная выветриванием серная кислота каким-либо путём не связывается, то энаргит окисляется в сульфат меди и в мышьяковую кислоту с образованием серной

кислоты, однако, при этом основные клиноклазиты не образуются. Раствор, содержащий сульфат меди, действует более растворительно на минеральный агрегат вышеуказанного состава, чем раствор, содержащий сульфат железа.

На оксидацию содержания двухвалентного железа растворов, из металлов переменной валентности, оказывают сильное воздействие медь и марганец. Совместное присутствие меди и марганца замедляет оксидацию двухвалентного железа в значительной мере, вследствие различий в окислительно-восстановительных потенциалах отдельных систем.