shows in a marked degree the property of hydrolysis common to ferric salts.

Summary.

The main conclusions from the above experiments may be thus summarized.

1. Precipitated ferrous sulphide does not react with zinc hydroxide in the cold, or at boiling temperature, and only slowly at 160°, the products being colorless ferrous hydroxide and zinc sulphide.

2. In general, the statement that ferric salts give a mixture of ferrous sulphide and sulphur, when precipitated in alkaline solution by an alkaline sulphide is erroneous; the product is ferric sulphide, which reacts with zinc hydroxide, rapidly in the cold, instantly on boiling, to form ferric hydroxide and zinc sulphide.

3. Alkaline polysulphides precipitate ferrous salts as ferric sulphide.

4. Ferric sulphide readily hydrolyzes into ferric hydroxide and hydrogen sulphide at 100°.

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EXPERIMENTS ON THE ACTION OF VARIOUS SOLUTIONS ON PYRITE AND MARCASITE

BY H. N. STOKES.

The experiments described in this paper from part of an unfinished investigation undertaken by the writer before his transfer from the U. S. Geological Survey to the Bureau of Standards. While the work is by no means complete, the results would appear to have some geological significance and are published now in the hope that they may contribute somewhat to an understanding of the formation and decomposition of sulphides. As the writer will be unable to pursue the subject further, he hopes that the work may be continued and enlarged by other chemists working along geological lines.

Without attempting to discuss the geological bearings, the results may be briefly summarized as follows : Pyrite and marcasite are decomposed by circulating alkaline waters which leave hematite or hydrated ferric oxide and carry away the sulphur in the form of alkali sulphides and thiosulphate. The sulphides may react in another place with metallic salts giving sulphides ; the thiosulphates may either remain unchanged or may react with copper or silver compounds, giving sulphides of these metals and alkali sulphates. This conversion of pyrite into hematite occurs in the absence of free oxygen ; the occurrence of ferric oxides as transformation products of pyrite is therefore not in itself a proof of the action of aerated water or other oxidizing agents.

Pyrite and Marcasite with Cupric Salts in Presence of Alkali Bicarbonates.—Cupric carbonate is not entirely insoluble in solutions of alkali bicarbonates ; in fact, strong bicarbonate solutions readily dissolve it to a blue solution. The solubility of cupric carbonate, however, is not essential to its reaction with pyrite and marcasite, as these are attacked by the alkaline solution itself, as will appear below.

The pyrite and marcasite used in the following experiments were finely ground and carefully purified by washing with ether to remove sulphur, digesting with hot dilute hydrochloric acid to remove ferric oxide, washing with dilute hydrochloric acid and water in an atmosphere of carbon dioxide and drying *in vacuo*[1]. The material was then transferred to the tube in which the experiment was to be made, the solution added, the air replaced by carbon dioxide and the tube sealed. In this way all oxidation was prevented.

About 0.2 gram marcasite was heated in a sealed tube filled with carbon dioxide for 14 hours at 160–170° with an 8 per cent. solution of cupric chloride to which potassium bicarbonate had been added to complete resolution of the carbonate. The solid product was chocolate-brown, evidently from the presence of ferric oxide. The quantitative analysis of the solid and solution, which was made with the view of excluding the action of the air, and after making allowance for the small residue of undecomposed marcasite, which was determined, showed that 25.04 per cent. of the total sulphur had been oxidized to sulphuric acid. The equation

$$2FeS_2 + 6CuCO_3 + 2KHCO_3 = 3Cu_2S + Fe_2O_3 + K_2SO_4 + 8CO_2 + H_2O,$$

requires the oxidation of 25 per cent.

0.2 gram carefully prepared pyrite, treated in a similar manner and heated 23 hours at 180°, showed that 26.7 per cent. of the sulphur had been oxidized to sulphuric acid. The equation is the same as above, and the agreement with the theoretical is as close as could be expected.

An experiment with marcasite and solution of cupric carbonate in ammonium bicarbonate was carried out at 100° for 18 days. While the decomposition was incomplete the formation of ferric oxide and sulphuric acid was confirmed.

Marcasite with Silver Carbonate and Potassium Bicarbonate.—Marcasite heated with silver carbonate and potassium bicarbonate for 22 hours at 180° gave a residue containing silver sulphide and ferric oxide, while the solution contained sulphate and was free from other sulphur acids.

Marcasite with Lead Carbonate and Alkali Carbonate or Bicarbonate.— One gram marcasite, 2 grams pure lead carbonate, 2 grams pure dry sodium carbonate and 20 cc. water were heated in a sealed tube filled with

[1] See U. S. Geol. Survey Bulletin No. 186, p. 20.

carbon dioxide for 24 hours at 180°. The insoluble product contained crystals of galena. The filtrate was divided into two equal portions. The first portion, on heating with hydrochloric acid gave a precipitate of sulphur, while only a trace of barium sulphate was obtained. The second portion, after oxidation with bromine water gave an abundant barium sulphate precipitate, which was weighed. The insoluble residue was freed from the excess of lead carbonate by boiling with acetic acid in a current of carbon dioxide, to prevent oxidation of any unchanged marcasite and consequent precipitation of lead as sulphate. In the residue which remained the lead sulphide was oxidized and weighed as sulphate. The atomic ratio of sulphur in solution to sulphur in lead sulphide was 2:13.43 or nearly 2:14. The behavior of the solution, which deposited sulphur on acidifying and contained sulphate only after oxidizing indicates the presence of thiosulphate. This and the above ratio agree with the equation :

$$8FeS_2 + 14PbCO_3 + Na_2CO_3 = 14PbS + 4Fe_2O_3 + Na_2S_2O_3 + 15CO_2.$$
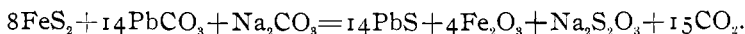
The amount of decomposed marcasite was calculated from the sulphur in solution plus that as lead sulphide, from which it appeared that the atomic ratio of sulphur in solution to iron in the decomposed marcasite was 2 : 7.73, or nearly 2 : 8 as required by the equation.

It will be observed that a marked difference exists between the behavior of copper and silver carbonate and that of lead carbonate, in that in the case of copper and silver, sulphate exclusively is found, while in the case of lead the product is thiosulphate with only a trace of sulphate. The explanation of this is to be found in the well known fact that copper and silver salts easily decompose thiosulphates on heating, giving metallic sulphide and sulphate[1] while lead salts are without action on thiosulphates. Hence it is likely that thiosulphate is a primary product of the reaction in each case. The reaction of the metallic carbonates with pyrite and marcasite in presence of alkali carbonate solutions is still better exemplified by the behavior of zinc carbonate.

Pyrite and Marcasite with Zinc Carbonate and Potassium Bicarbonate.— These experiments were made in essentially the same manner. Zinc sulphide being white, it was easy to distinguish the ferric oxide by its color. The solutions were carefully analyzed, bearing in view the possibility that alkali sulphide, polysulphide, thiosulphate, sulphite and sulphate might be present. It is unnecessary to detail the somewhat complicated procedure employed and it may be merely stated that by treatment of different aliquot portions of the solution with cadmium hydroxide to remove sulphide, determining sulphuric acid in one portion directly and in another after oxidation, making an iodine titration with a third and deter-

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[1] $CuS_2O_3 + H_2O = CuS + H_2SO_4$
$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$

mining the thiosulphate in another by heating with silver nitrate, it was found that sulphides, sulphites and sulphates were absent and that the total sulphur in solution was present as thiosulphate, which, moreover, gave the characteristic reactions. The residue was not further examined than to determine that all the pyrite or marcasite was decomposed, and that zinc sulphide and ferric oxide, mixed with excess of zinc carbonate were left. The equation in all probability is

$$8FeS_2 + 14ZnCO_2 + 2KHCO_3 = 14ZnS + 4Fe_2O_3 + K_2S_2O_3 + 16CO_2 + H_2O$$
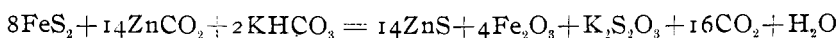
Action of Alkali Solution Alone on Pyrite and Marcasite.

In the above experiments the action of the alkaline solution on the pyrite or marcasite took place in the presence of a carbonate of a metal (Cu, Ag, Pb, Zn) capable of forming a stable insoluble sulphide. In the case of zinc and presumably in that of the other metals also, the reaction proceeded to completion, the final product being ferric oxide and metallic sulphide and in solution either thiosulphate or sulphate. In the following experiments, some light is thrown on the nature of the reaction.

One gram carefully prepared marcasite powder, 3 grams dry sodium carbonate and 30 cc. water were sealed in a bomb tube in which the air had been replaced by carbon dioxide, and heated 22 hours at 185°. The contents were filtered. The filtrate had a yellowish color, due to the presence of alkali polysulphides, and after removal of these by cadmium chloride, was found to contain much thiosulphate.

One gram marcasite powder, 4 grams potassium bicarbonate and 40 cc. water were similarly treated. The filtrate contained sulphide and polysulphide and after removal of these by cadmium chloride gave 0.0144 gram $K_2S_2O_3$ by titration and 0.0150 gram $K_2S_2O_3$ by direct gravimetric determination as silver sulphide.

One gram marcasite, 4 grams potassium bicarbonate and 25 cc. water heated in the sealed tube 16 days at 100° gave sulphide and 0.0083 gram $K_2S_2O_3$ by titration and 0.0080 gram gravimetrically.

One gram marcasite, 3 grams dry sodium carbonate and 30 cc. water were heated 30 hours at 180°. The yellow solution was found to contain 0.0119 gram $Na_2S_2O_3$ and for 1 mol. $Na_2S_2O_3$ there were 4.38 mols. Na_2S and 2.51 mols. Na_2S_2.

One gram pyrite powder heated as above with 3.5 grams dry sodium carbonate and 35 cc. water gave 0.0072 grams $Na_2S_2O_3$, and for 1 mol. $Na_2S_2O_3$ there were 3.30 mols. Na_2S and 1.05 mol. Na_2S_2.

In the reactions in which the metallic carbonates are absent, the amount of thiosulphate is much less, while alkali sulphide and polysulphide appear. The reaction is undoubtedly complicated and in part reversible. The experiments throw some light on what occurs, however. The formation of ferric oxide with zinc carbonate in an alkaline solution, in the

absence of oxidizing agents, shows that the pyrite and marcasite may be regarded as ferric compounds. We may regard them as ferric sulphide containing an excess of sulphur, viz. as Fe_2S_3. S.

It is well known that free sulphur reacts with alkalies giving sulphide and thiosulphate, thus :

(1) $4S+3Na_2CO_3 = 2Na_2S+Na_2S_2O_3+3CO_2$.
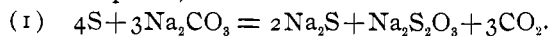
A further reaction would be that between sulphur and the sodium sulphide thus generated :

(2) $S+Na_2S = Na_2S_2$.
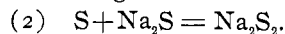
The experiments do not show which of the polysulphides are found, but it will suffice to assume that Na_2S_2 is present. A third reaction would be that between the ferric sulphide portion of the molecule and the alkali :

(3) $Fe_2S_3+3Na_2CO_3 = Fe_2O_3+3Na_2S+3CO_2$.
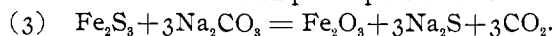
The third reaction is undoubtedly easily reversible and in fact does not proceed to any great extent, if the ferric oxide is kept in contact with the generated alkali sulphide. The sulphide and polysulphide occurring in the solution come mainly, and the thiosulphate entirely from the excess of sulphur in the pyrite and marcasite and it is clear that as several independent reactions are involved there can be no simple relation between the quantities of each product formed; an indeterminate portion of the excess of sulphur acts according to (1) and the remainder according to (2).

As long as the decomposition products remain in contact no very considerable amount of ferric oxide can be formed. If, however, the sulphide in solution is continually removed, either by circulation or by precipitation, the transformation of the ferric sulphide into ferric oxide will eventually be complete. This is what occurs in the above experiments with copper, silver, lead and zinc carbonates. The removal of the soluble sulphides by continually supplying fresh alkaline solution can not be easily effected in the laboratory, where comparatively high temperatures and small volumes have to be used. In nature, however, this may be easily realized and the transformation of pyrite into hematite effected without the aid of oxidation. Thiosulphates are occasionally found in mineral waters and while these may be formed by the action of alkali carbonates or alkali sulphites on free sulphur, or by the action of free oxygen on waters carrying sulphides in solution[1] it is an hypothesis worthy of consideration that they may in part originate from the action of deep seated, oxygen-free alkaline waters on pyrite.

While the removal of the soluble sulphides by continually renewed fresh solution is not experimentally available a third method remains, namely, the volatilization of the sulphur as hydrogen sulphide. Alkali sulphides do

[1] $2Na_2S+4O+CO_2 = Na_2S_2O_3+Na_2CO_3$
$Na_2S_2+3O = Na_2S_2O_3$
$Na_2S_5+3O = Na_2S_2O_3+3S$
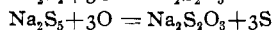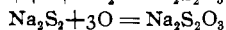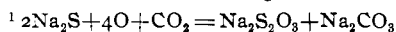
not liberate free hydrogen sulphide on boiling; if, however, carbon dioxide is present, this decomposes the sulphide, the reaction, however, soon coming to equilibrium unless the hydrogen sulphide is removed. This can be effected at higher temperatures in closed vessels, free from air, by the presence of an absorbent entirely outside the liquid.

0.2 gram carefully purified marcasite powder was placed in a 20 cc. platinum crucible with one gram potassium bicarbonate and a little water. The crucible was placed within a platinum digester of 50 cc. capacity, the lid of which could be clamped down air-tight and on the bottom of which, outside the crucible, some lead carbonate was placed. The air in the apparatus was replaced by carbon dioxide and the lid at once closed. The digester was placed under water in an autoclave and heated 7 days at 180°-200°. On opening, the marcasite was found to be completely converted into scaly hematite, while the lead carbonate outside the crucible and therefore never in contact with the solution had been converted into acicular crystals of galena, the excess of carbonate being crystallized to cerussite.

In a similar experiment with pyrite, in which the lead carbonate was replaced by cuprous oxide the pyrite was converted into hematite and the cuprous oxide into chalcocite, while the solution within the crucible contained thiosulphate.

In a third experiment with the same apparatus, pyrite was used and the absorbent consisted of a series of discs of copper gauze placed on top of the crucible. After heating the digester under water in the autoclave for eight days at 200° it was found that water had leaked into the digester, covering the gauze, which was covered with crystals of chalcocite as much as 5 mm. long. The pyrite had been converted partly into hematite but mainly into magnetite, which under a low magnifying power showed well developed octahedra, black and brilliant and strongly magnetic. The formation of magnetite in this case is doubtless to be ascribed to the hydrogen liberated by the action of the hydrogen sulphide on the metallic copper.

From the above experiments we may conclude that pyrite and marcasite can be completely converted into hematite by alkaline solutions, without the intervention of oxygen, provided the generated sulphides are removed by circulation. The solution, carrying sulphide and thiosulphate, coming in contact with soluble or insoluble salts of copper, silver, lead or zinc, will have the sulphide removed, and in the case of copper or silver, the thiosulphate will give rise to a further amount of sulphide, the equivalent of sulphate taking its place.

Pyrite and marcasite are not the only sulphides which can generate thiosulphate in the above manner. Covellite was heated with 10 per cent. sodium carbonate in a sealed tube filled with carbon dioxide for 22

hours at 180°. The solution contained abundant sulphide, polysulphide and thiosulphate. The reactions, in a simplified form may be thus expressed:

$$8CuS + 3Na_2CO_3 = 4Cu_2S + 2Na_2S + Na_2S_2O_3 + 3CO_2$$
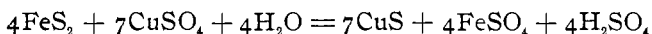
and

$$2CuS + Na_2S = Cu_2S + Na_2S_2.$$
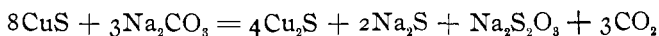
About one-fourth the thiosulphate required by the first equation was found.

Action of Neutral Solutions of Metallic Salts on Pyrite and Marcasite.

Action of Cupric Salts.—In a former paper[1] I have shown that when pyrite is heated with neutral cupric chloride solution at 200° in the absence of air, the sulphur is completely oxidized to sulphuric acid. The reaction between pyrite and marcasite and cupric sulphate also results in the formation of sulphuric acid, but the sulphur is not completely oxidized, a portion remaining in the form of sulphides of copper. According as cuprous or cupric sulphide is formed, we may have the equations:

$$5FeS_2 + 14CuSO_4 + 12H_2O = 7Cu_2S + 5FeSO_4 + 12H_2SO_4$$

in which 30 per cent. of the sulphur is oxidized, or

$$4FeS_2 + 7CuSO_4 + 4H_2O = 7CuS + 4FeSO_4 + 4H_2SO_4$$

in which 12.5 per cent. of the sulphur is oxidized.

In reality the action is more complicated, the cuprous ion being involved[2]. Cuprous sulphide is itself attacked by cupric sulphate, while cupric sulphide, at least in the form of covellite, is very resistant. The actual result of the experiments shows that the amount of sulphur oxidized to sulphuric acid lies between these extremes, so that it is likely that both reactions take place.

Carefully purified marcasite was heated at 180° for 20 hours with an accurately determined amount of neutral 10 per cent. cupric sulphate solution, under rigid exclusion of air, and the increase of SO_4 in the solution, as well as the composition of the residue determined. After making allowance for unaltered material, 18.4 per cent. of the sulphur was found to be oxidized.

In an exactly analogous experiment with pyrite 20.65 per cent. of the sulphur was oxidized.

An experiment with marcasite and neutral 10 per cent. cupric sulphate solution at 100° continued for 18 days, showed that 23.8 per cent. of the sulphur of the decomposed mineral was oxidized.

Pyrite and Marcasite with Neutral Lead Chloride.

Purified pyrite and marcasite were heated with pure lead chloride and

[1] U. S. Geol. Survey Bulletin 186, p. 44.
[2] Journal of Economic Geology 1, 648 (1906).

water in sealed tubes filled with carbon dioxide for 12 hours at 180°. The solid product contained large quantities of galena and lead sulphate, the latter being decomposed and its SO_4 extracted by treatment with sodium carbonate solution.

The reaction is therefore presumably :

$$4FeS_2 + 7PbCl_2 + 4H_2O = 7PbS + 4FeCl_2 + H_2SO_4 + 6HCl.$$
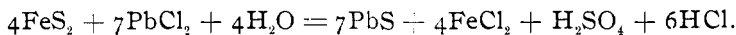
From these experiments it would seem that the formation of free sulphuric acid through the action of neutral, air-free copper and lead solutions on pyrite and marcasite is a factor which can not be neglected.

Note on the Identification of Chalcocite.

Chalcocite is readily attacked by ferric salts thus :

$$Cu_2S + 2FeCl_3 = CuS + CuCl_2 + 2FeCl_2.$$
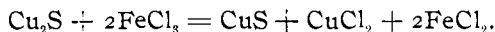
The CuS thus formed shows the blue color of covellite. A fragment of chalcocite boiled for a moment with 10 per cent. ferric chloride solution acidified with hydrochloric acid becomes blue. The color appears to particular advantage on compact smooth chalcocite, but the rough mineral also becomes decidedly blue. A gray coating on chalcopyrite took on a deep indigo-blue color. The same effect is produced, but not as satisfactorily, by boiling with 1–1 hydrochloric acid or allowing to stand a short time with concentrated hydrochloric acid, but this is apt to dissolve the coating completely. Enargite is entirely unaltered in appearance by the above treatment[1].

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THE ELECTROLYTIC DEPOSITION OF NICKEL-ZINC ALLOYS.

BY EUGENE P. SCHOCH AND ALCAN HIRSCH.

Some time ago, while making some general experiments on the electrolytic deposition of alloys, we were surprised to find that, although zinc has a greater electrolytic solution tension than nickel, yet a bath which contains much more nickel than zinc yields an alloy which contains much more zinc than nickel. This fact appeared worthy of study and the paper presented below embodies the results which have been obtained so far.

The apparatus and arrangement used were as follows :— a paraffined wooden trough 49 x 13 x 10 cm. was filled with the electrolyte to a depth of about 7 cm. The anodes were placed at the ends of the trough, the active surface of each anode being 13 x 7 cm. The cathode was a cylinder of thin sheet metal with its axis vertical ; it was placed approximately midway between the anodes. Its active surface was as nearly 1

[1] Knop. N. J'b. 1861, S. 533.