

NOTES AND NEWS

A METHOD FOR REMOVING IRON OXIDE COATINGS FROM MINERALS¹

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This paper deals with a method for removing the iron oxide coating which is often found on the surface of finely divided uncrushed mineral grains of sedimentary materials. These coatings render petrographic studies more difficult and less accurate, lead to the contamination of x -ray patterns, and interfere with accurate specific gravity determinations and separations, especially in the case of the more finely divided materials. Acids have been used for the removal of this ferric oxide, but the concentration necessary is so great that in many cases minerals other than the ferric oxide are seriously attacked. The writers found, in attempting to remove ferric oxide from soil colloids, that, by introducing hydrogen sulfide into a water suspension of the colloid, the free ferric oxide is quickly changed to iron sulfides which dissolve readily in dilute HCl. The simplicity and effectiveness of the method led to its application in the field of pure mineralogy.

A review of the literature shows that hydrated ferric oxide has been used for more than sixty years as an absorbent for H_2S in the purification of coal gas. Wright,² in 1883, reported that $Fe(OH)_3$ suspended in water turned black when H_2S was introduced, Fe_2S_3 , FeS , and S being formed. Allen et al.³ showed that these iron sulfides are completely soluble in cold dilute HCl. Recently, Pearson and Robinson⁴ summarized the literature and concluded that a mixture of sulfides is formed.

ACTION OF HYDROGEN SULFIDE ON IRON OXIDE

Preliminary tests with H_2S -saturated water suspensions of 100-mesh limonite showed rapid formation of black iron sulfides which

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² Wright, L. T., Some Notes on Hydrated Ferric Oxide and Its Behavior with Hydrogen Sulfide: *Jour. Chem. Soc.*, vol. 43T, pp. 156-163, 1883.

³ Allen, E. T., Crenshaw, J. L., Johnston, J., and Larsen, E. S., Mineral Sulfides of Iron: *Amer. Jour. Sci.*, (4) vol. 33, pp. 169-236, 1912.

⁴ Pearson, T. G., and Robinson, P. L., The Reaction between Monohydrated Ferric Oxide and Hydrogen Sulfide at 100°: *Jour. Chem. Soc.*, pp. 814-823, 1928.

dissolved readily in cold 0.05 *N* HCl. Most of the original iron oxide was dissolved by this treatment. To determine whether or not the acidity of the H₂S solution (about pH 4, slightly less acid than carbonated water) dissolved the iron oxide before it was changed to sulfides, the H₂S solution was neutralized with NH₄OH before being used. This neutralized H₂S solution was even more effective than the acid H₂S solution, which indicated that the sulfides are formed directly as a result of a surface reaction.

In further tests, samples (50 mg. each) of finely powdered limonite and hematite were shaken with 200 cc. of H₂S-saturated water adjusted to pH 7 with NH₄OH. The iron sulfides formed were dissolved in 0.05 *N* HCl and the iron in solution determined. Shaking for one-half hour with subsequent HCl treatment dissolved 90% of the limonite but only 8.5% of the hematite. After one hour of shaking, all of the limonite dissolved but only 9% of the hematite, indicating that the amount of surface exposed by the crystalline hematite was not sufficient for rapid action of the H₂S.

Samples of crystalline hematite and goethite and ordinary limonite were then prepared in which the particle size was 0.0001 mm. and less in diameter. The goethite and hematite were ground in a tool steel ball mill. Suspensions containing 50 mg. of these materials in 200 cc. of H₂S-saturated water adjusted to pH 7 with NH₄OH were shaken for one-half hour. The iron sulfides formed were dissolved in cold 0.05 *N* HCl, the solution filtered and the iron determined in the filtrate. In the case of goethite and limonite all of the material had dissolved, but in the case of the hematite 7% of the sample remained undissolved. Upon analysis, 40% of this residue was found to consist of SiO₂, indicating the presence of an iron silicate, the iron of which did not react readily with the H₂S. These tests show that iron oxide, hydrated and unhydrated, when sufficiently finely divided reacts quickly with H₂S to form sulfides which are readily soluble in 0.05 *N* HCl.

ACTION OF HYDROGEN SULFIDE ON IRON IN ROCKS AND MINERALS

In order to find out if the H₂S treatment would have an appreciable effect on ferric iron as found in igneous rocks and especially in silicate form, 0.1 gram samples of biotite and basalt and a 0.2

gram sample of granite, all ground finer than 100-mesh, were shaken for several hours with 300 cc. of H_2S -saturated water solution adjusted to pH 7 with NH_4OH . At various intervals, 10 cc. portions of the suspensions were removed and treated with 10 cc. of 0.1 *N* HCl and then filtered quickly. After expelling the H_2S and oxidizing with ammonium persulfate, the filtrates were tested for iron colorimetrically with KCNS. Check samples of the mineral powders were treated with water alone instead of the H_2S solution. Samples of these suspensions were treated with HCl, filtered, and tested in exactly the same way as the others. It was found that the H_2S treated samples gave only a slight test for iron, the same as the check samples, indicating that what little solution of iron took place was due to the direct action of the HCl on the original minerals, and that the H_2S treatment does not readily affect iron in the silicate form.

DETAILS OF PROCEDURE FOR REMOVING FERRIC OXIDE

Place a one to ten gram sample of the powdered mineral in a 500 cc. Erlenmeyer flask with 200 to 300 cc. of distilled water. Saturate the suspension with hydrogen sulfide which is bubbled in from a tank or generator. This takes about 10 or 15 minutes. Quickly add about 5 cc. of *N* NH_4OH and stopper immediately with a rubber stopper. Shake with a mechanical shaker for about an hour, or intermittently by hand for a somewhat longer period. Acidify with 0.1 *N* HCl, adding an excess of about 50 cc. so as to completely dissolve the iron sulfides. Filter immediately so as to avoid action of the acid on the other minerals. Wash several times with 0.05 *N* HCl. If desired, the amount of free iron oxide removed may be determined by an analysis of the filtrate and washings. The mineral residue on the filter paper is always contaminated with free sulfur which may be removed in the following way: Wash twice with 95% ethyl alcohol to remove water, then three times with a solution consisting of one volume of carbon bisulfide and two volumes of 95% alcohol to remove the sulfur, and finally twice with the alcohol to remove the carbon bisulfide.

The residue is then dried, thus completing the cleaning process. In place of filtering and washing on a filter paper, this portion of the procedure may often be conveniently performed by washing by decantation using a centrifuge if necessary.

CONFIRMATORY TESTS WITH THE PROCEDURE

In order to check the method further, samples⁵ of feldspar, baddeleyite, and quartz powder, the surfaces of which were coated with considerable iron oxide as revealed under the microscope, were subjected to the hydrogen sulfide treatment. After the treatment, the minerals, under the microscope, appeared relatively free of iron oxide but otherwise were unaffected. An appreciable amount of iron was found in the extracts, but distinct tests for other constituents were not obtained. This showed that the iron oxide coatings had been removed without noticeably affecting the minerals in question.

Two samples of sandstone powder⁶ which contained some feldspar and the heavy minerals—zircon, tourmaline, and apatite—were given the hydrogen sulfide treatment. There had been difficulty in making specific gravity separations of these rock powders, because the iron oxide coating on the feldspar and quartz grains increased their specific gravity so much that they would not separate sharply from the heavy minerals. It was not permissible to use strong acids to remove this coating because of the solubility of the apatite and feldspar. After the hydrogen sulfide treatment, however, the quartz and feldspar were easily separated from the heavy minerals and, upon microscopic examination, were found to be practically free of iron oxide.

Since apatite is one of the easily soluble minerals encountered in making specific gravity separations, it seemed desirable to determine just how much it is affected by the hydrogen sulfide treatment. Accordingly, a known amount of 100-mesh apatite was added to a sample of sandstone powder, which was then given the hydrogen sulfide treatment. After this treatment, a specific gravity separation was made and practically all of the apatite was recovered. The hydrogen sulfide extract contained an appreciable amount of iron but only a trace of calcium, showing that the apatite had hardly been attacked at all. A microscopic examination of the treated apatite showed very little if any rounding of the crystal fragments when compared with an untreated sample.

The presence of free iron oxide may also obscure correlations between the results of chemical analysis and optical determina-

⁵ Samples furnished by Dr. R. C. Emmons, Department of Geology.

⁶ Acknowledgment is due to Mr. Tyler and Mr. Marsden of the Department of Geology for furnishing the samples and giving information regarding them.

tions of minerals. It is desirable to distinguish between free iron oxide and combined iron, since the latter affects the refractive index of a mineral. In some work⁷ on the correlation between the optical properties and chemical composition of different varieties of supposedly pure muscovite, treatment with hydrogen sulfide removed 0.3 to 1.5% of free iron oxide. After this treatment, a better correlation was obtained between the refractive index and chemical composition of the muscovites. The hydrogen sulfide treatment can probably be used to advantage in similar investigations of many other minerals.

Hematite, unless extremely finely divided, is not readily affected by the hydrogen sulfide treatment. A sample of feldspar containing relatively coarse crystals of hematite was treated with hydrogen sulfide, but not much of the free iron oxide was removed. The method, while well adapted for the removal of finely divided iron oxide, is not suitable for the removal of the larger crystals. These may be removed by specific gravity separation.

SUMMARY

It was found that the iron oxide coating of minerals can be easily removed if a water suspension of the minerals is first treated with hydrogen sulfide. This treatment changes the finely divided iron oxide to iron sulfides which dissolve quickly in 0.05 *N* hydrochloric acid. Other minerals such as silicates and apatite are not appreciably affected, although carbonates would be. The method has much useful application in optical and specific gravity investigations of minerals.

⁷ Work by Garth Volk in the Departments of Geology and Soils, University of Wisconsin.